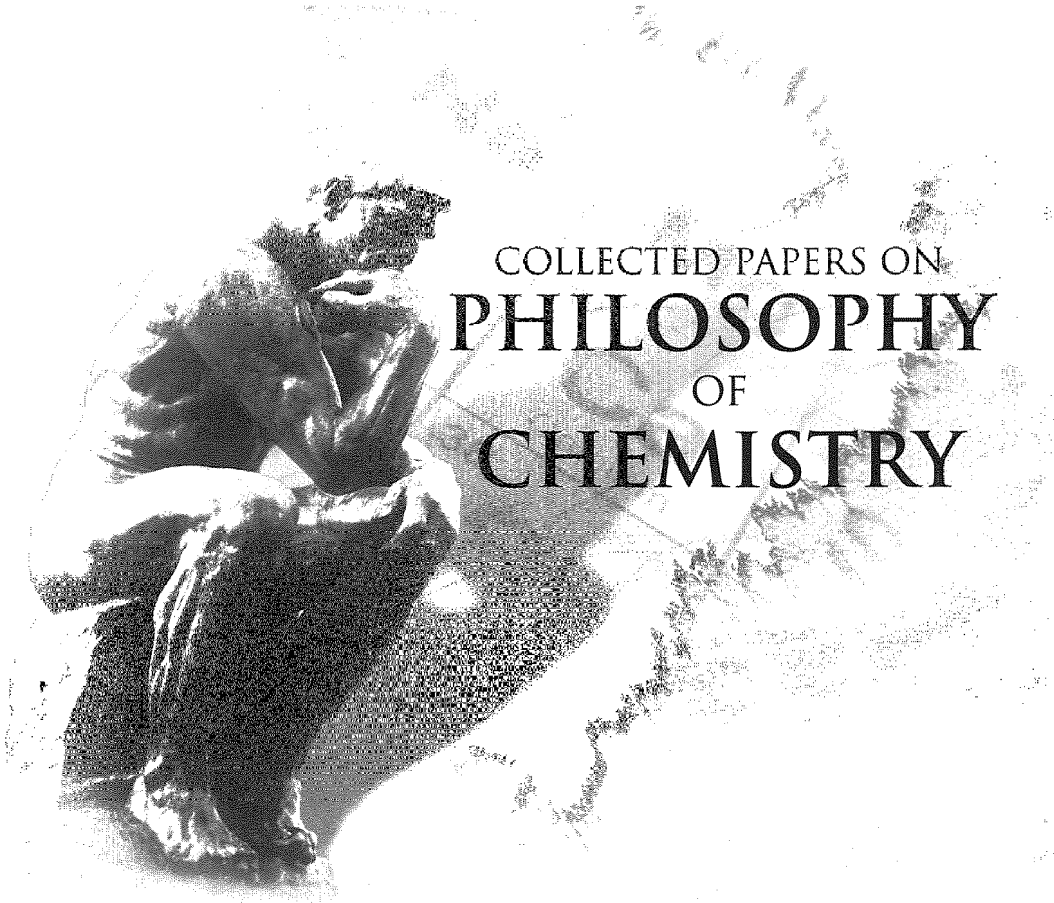

COLLECTED PAPERS ON PHILOSOPHY OF CHEMISTRY

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Dedication

I dedicate this book to my mother Ines Scerri and to the memory of my father Edward Scerri.

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I would like to acknowledge the help of all my mentors, colleagues and students and in particular the late Heinz Post who supervised my PhD thesis at King's College, University of London, which I completed in 1992.

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Eric Scerri
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General Introduction to the papers

Eric Scerri

One of my earliest memories about my education concerns a conversation I had with an older boy at my school when I was about six or seven years old. The older boy told me that he was studying a subject called history. Of course I was rather intrigued by this, but the boy rudely informed me that I was too young to even understand what it was about. I don't know whether this early incident piqued my interest in history or whether I just had an aptitude for the subject but when I later went to secondary school in London, history became the only subject in which I really excelled. When exams came round we would each be provided with five or six blank sheets of paper in addition to a list of questions. Those of us who were good at history would take great pride in very quickly filling our allotted sheets and promptly walking to the front of the class to collect extra sheets of paper. But only one sheet was allowed at a time. I think I can once recall filling a total of fourteen sheets of paper with the details of the agrarian and industrial revolutions that took place in eighteenth and nineteenth century England.

Unfortunately all such acts of bravado, at least on my part, came to an end the following year because we were expected to choose just three subjects to pursue at Advanced level and I chose chemistry, physics and mathematics. This meant that from the tender age of fifteen I was destined to never again study history. As for philosophy, this would not even have been an option had I chosen to go the way of the humanities. Unlike in the French system where philosophy is almost synonymous with the humanities, the study of philosophy in the British system was completely unheard of at least in the vast majority of secondary schools.

After struggling for two years in my chosen A level subjects, I applied to do chemistry at university. There again British undergraduate education was very much about depth at the expense of breadth. There were absolutely no required subjects from the humanities or even general studies for science students. In fact it was something of an effort to convince my tutors to allow me to take units in astronomy, geophysics and even physics.

Somehow I survived this process and even got into Cambridge to study theoretical chemistry towards which I had gravitated largely because of its more fundamental, perhaps even philosophical flavor. Now finally something inside of me began to rebel against the deprivation from history and philosophy and I suppose the humanities in general. I could not buckle down to accepting the "shut up and calculate philosophy" that students are advised to adopt when it comes to doing quantum mechanics. Eventually my advisor, David Buckingham, suggested that I might take some of my more philosophical ruminations to the department of history and philosophy of science in Free School lane. There my essay was looked at by Gerd Buchdahl and Mary Hesse. Buchdahl even interviewed me and spent most of the time talking about Kant, something I knew absolutely nothing about then and very little about even now. But a switch to the study of history and philosophy of science was not to be, at least not at that stage.

I continued to toil with my very specific problem on the quadrupole moments of small molecules and I left at the end of that same academic year. I then spent the next two years carrying out research in experimental physical chemistry at the University of Southampton, to which I was even less suited than work on a specific problem in theoretical chemistry.

Finally I had used up all my research grant money and was forced to go out into the real world. Well not quite the real world since I began teaching in secondary schools. Living as I was in Central London by this time I began frequenting the library at Chelsea College in the fashionable King's Road. This library was filled with books that dealt with the historical and fundamental aspects of all the sciences and it was not long before I made an application to do some part time research towards a PhD.

I was interviewed by the head of the History and Philosophy of Science department, Heinz Post, as well as Michael Redhead the philosopher of physics. They took little time to convince me that I was not really equipped to carry out research into the foundations of physics but Post in particular was generous enough to suggest my working in what seemed at the time the less glamorous area of the foundations of chemistry. After thinking about this for a couple of weeks I began

recalling some difficult questions, which come up in the course of teaching chemistry. One in particular had led me to many conversations with colleagues, none of whom seemed to share my wanting to get to the bottom of the question. This issue concerns the electronic configurations of some elements. As is well known, starting with potassium, the differentiating electron occupies a 4s orbital rather than a more expected 3d orbital. To make matters worse, when such an element as scandium is ionized, the first two electrons are not removed from the 3d orbitals but from 4s.

So as Heinz Post put me to work on understanding atomic physics and the nature of the orbital approximation, the thing that kept me going, especially at the beginning, was the prospect of being able to unravel the apparent 4s/3d paradox. It quickly became clear that little work had been carried out in the foundations of chemistry or the philosophy of chemistry. From time to time I would go to conferences and tell people that I was doing research into the philosophy of chemistry. The response was usually that this sounded very interesting and that there seemed to be no such recognized field of study whereas the other two natural sciences, physics and biology, had their own well-established sub-disciplines of philosophy of physics and of biology respectively.

I decided to try to redress this imbalance in whatever way I could. Soon afterwards I found myself quite literally at what might be called 'the right place at the right time'. At a festschrift for Heinz Post in London, I found myself seated next to the late Annie Kuipers the managing editor of Kluwer journals in philosophy and the publisher of Heinz's festschrift.[1] As Post's most recent, and as it turned out, his last PhD student, I had rather generously been invited to submit an article to this volume alongside some prominent names in history and philosophy of science. Annie Kuipers naturally asked me what I was working on and when I told her she immediately replied, "We should start a journal for the Philosophy of Chemistry". It was left to me to write several proposals and to gather an editorial board. Three years later the journal *Foundations of Chemistry* was finally launched and is now in its tenth year of continuous publication.

I was also at the right place at the right time because other people who had been independently working on various aspects of what became

philosophy of chemistry started to come forwards. The process was initially catalyzed by Michael Akeroyd in Yorkshire, England. I should also mention a group of chemical educators in Germany that had already started publishing a newsletter that eventually became the other current journal in the field, namely *Hyle* which is edited by Joachim Schummer. Gradually we began to make our presence felt at the major meetings in history and philosophy of science. These days no PSA meeting is complete without the inclusion of two or three sessions devoted to the philosophy of chemistry. We seem to have come quite a long way since the first international meetings began to take place in 1994.[2]

The present volume

That's probably enough personal reminiscence for the time being. I turn now to the contents of this volume. At the suggestion of the publisher and some reviewers, the papers are arranged thematically rather than chronologically.

The opening section is on the question of philosophy of chemistry as a whole, and on the question of reduction. I should mention that the collection does not cover the entire field of philosophy of chemistry.[3] However it does cover what I think is the most fundamental question, namely the alleged reduction of chemistry to quantum mechanics.

Now there are several ways of addressing the reduction question which are briefly examined in what follows. Suffice it to say that the widespread belief that chemistry does successfully reduce to physics and indeed that this is the paradigm example of a successful reduction, has probably been the main reason for the previous neglect of the philosophy of chemistry. It is not difficult to see why this has been the case. If chemistry is nothing but physics then all interesting and deep questions are addressed by the reducing science and the philosophical study of the reduced science is left to wither away as indeed it had done.

This view has been partly reinforced by the triumphant proclamations made by a number of 20th century physicists such as one by Fritz London which dates from 1927,

"Now physics is capable of eating chemistry with a spoon."

But the reduction of the special sciences to physics had come under attack for general reasons not having much to do the details of chemistry. First of all, the putative reduction of the special sciences began to be regarded as another unfulfilled dream of the logical positivist program. Along with the move away from a formal logical approach to the philosophy of science, practitioners began to consider the specific details of theories, including their historical development. This was partly motivated by the historical turn initiated by Kuhn, Lakatos and Feyerabend and their simultaneous critiques of the logical positivist program. Even earlier Popper had emphasized the need to consider the details of the special sciences even if he did not always do so himself.

Another motivating factor from within philosophy itself was Quine's denial of the distinction between analytical and synthetic propositions. The consequence of Qunine's classic paper on the subject was the idea that there is no such thing as a 'first philosophy'. Instead, philosophy of science would need to appeal increasingly to scientific findings.

Then came the sociological turn which, for all its faults, contributed further to the examination of actual scientific practice rather than just an examination of the logical relationships between axiomatized versions of theories in the special sciences.[4]

But how exactly should one pursue a more naturalistic approach to the philosophy of chemistry? This is one area to which I hope to have made a small contribution. To put it simply, I have suggested carrying out an examination of the methodology that chemists and physicists actually use when trying to explain chemical phenomena from first principles. This accounts for the importance of the orbital approximation in my work, since this has been by far the most commonly used approach in theoretical chemistry.

But the denial of reduction among philosophers of science has, I believe, gone a little too far. It has become politically correct among philosophers to deny reduction period. This leads me to another point about reduction. The rhetoric among philosophers of science seems to be along the lines that a particular special science is or is not reduced, as though the outcome were a categorical black & white affair. This attitude may be something of a throwback to the former logical approach where such definite pronouncements were the currency. But in the more current

naturalistic climate the question of reduction, I suggest, should be regarded as one of degree rather than 'all or nothing'. And yet I have never seen this issue explicitly addressed in the philosophical literature on reduction.

There is one more general point concerning the section on reduction that I should mention. The work that I have concentrated upon may be described as addressing the epistemological side of the issue. After all I have mostly considered whether theories of chemical phenomena reduce to theories of physics. A skeptic might respond by pointing out that all I have established in denying the reduction of chemistry is the existence of a 'computational gap'. To such a skeptic the more interesting question is whether there is anything about chemistry *in principle* that renders it not susceptible to a reduction to physics. One might describe this as taking an ontological approach, which might also be regarded as addressing the more fundamental philosophical question. But how ought one to begin to address this deeper question?

There are a variety of opinions on this point. The majority of philosophers of science adopt a Quinean approach of obtaining their ontological conclusions from what modern scientific theories tell us. Ontology is read off the epistemology. One uses the findings of scientific theories to discover the furniture of the universe – the fundamental entities that populate it.[5] Others try to separate ontology from epistemology rather than making the former dependent on the latter.

Section A. Philosophy of Chemistry and the Question of Reduction

Let me now get to the papers themselves. The first of these is one that I co-authored with Lee McIntyre a philosopher of social science who has had a deep interest in the philosophy of chemistry for many years. The paper formed part of a special issue of the journal *Synthese* on the Philosophy of Chemistry which McIntyre and myself were invited to produce in the mid 1990s.[6] In this paper we tried to set out the main motivations, as we saw them, for why anyone might want to even consider the philosophy of chemistry. Now that I am able to comment on this paper with the benefit of hindsight I would like to emphasize that at least one of our claims may have been short-sighted. What McIntyre and

I insisted upon at the time was that all interest should be directed at what we called the epistemological reduction of chemistry. However, we went even further in saying that we took the ontological reduction of chemistry to physics as "almost a forgone conclusion". This uncritical acceptance of the ontological reduction of chemistry has subsequently been challenged, and correctly so, by two Argentinian philosophers of science who suggest that it is the ontological question which is of particular interest to philosophers in other areas and that we were wrong to take such an uncritical stance over this question.[7]

Turning to what we did concentrate upon, McIntyre and I stressed the need to consider reduction from the point of view of what can be strictly deduced from quantum mechanics in an ab initio manner. We tried to clarify the distinction between these kinds of calculations and so called semi-empirical work in which some experimental data is used to fix parameters. We also pointed out other variations even within strictly ab initio work and the desirability of including ab initio estimates of expected errors. We discussed the notion of calibrated ab initio calculations which are commonly carried out in the field and which do not represent genuine ab initio work, at least not to the most rigorous possible level.

We then turned from such discussions of quantitative reduction of chemical data to what we termed "conceptual reduction". We argued, as others have done before us, that many properties and quantities that are of interest to chemists such as bonding and composition only exist at a certain scale level. If one goes too far along the reductive reductive path, the very concept that one wants to explain ceases to have meaning.

We also discussed the notions of explanations and laws and whether they might have a different character in chemistry than they have in physics. We argued that the periodic law, for example, is somewhat different from laws in physics in that it is approximate. Nevertheless it is capable of embodying a tremendous body of information and is capable of making predictions as happened in the hands of Mendeleev who successfully predicted the properties of about 8 elements. On the question of explanations, we point out that atomic orbitals and electronic configurations are ubiquitous in modern chemistry even though neither of these concepts are rigorously valid from the perspective of quantum

mechanics. Atomic orbitals for example are mathematical constructs that may be defined with a considerable degree of latitude, as they frequently are in modern chemistry and physics. The upshot from this situation is that we may begin to speak about the autonomy of chemistry, which if true should consolidate the value of studying the philosophy of chemistry rather than merely attending to physics.

We examined the notion of supervenience and tried to construct some examples of chemical relevance. This notion which was especially popular in the 1990s was originally touted as a way out of the impasse that reduction seems to face. According to the supervenience thesis, if two systems are constructed in an identical manner from the same microscopic components we expect to observe the same macroscopic behavior. However, as the thesis continues, the same behaviour which occurs at a macroscopic level cannot be identified with identical micrsoscopic make-up in two systems. McIntyre and I focused on the property of smell as an example of macroscopic behavior and we tried to examine what supervenince might imply regarding the molecular aspects which give rise to smell.

Initially there was much interest in supervenience among philosophers who also invented different forms of supervenience which applied to various 'possible world scenarios'. These days interest appears to have waned a little and in fact the leading expert, Jagweon Kim, appears to have turned his back on the concept. The main worry is that even if one can establish a supervenience relationship between any two levels, there seems to be no way to establish that one level causes the other one and not vice versa. Putting this in different words, there appears to be a problem with trying to to ground physicalism so that we can claim that microscopic levels governs the macroscopic levels and not vice versa. Just to mention an aside, this would seem to open the door for emergence and the related concept of downward causation which is being discussed to a greater extent these days and which is addressed in the fourth of the papers in this section.

The question of the reduction of chemistry is usually addressed from the perspective of quantum mechanics as it was developed by Heisenberg and Schrödinger in the years 1925-26. It is interesting to go further back historically in order to examine the question from the point of view of

the earlier quantum theory of Bohr. This feat is attempted in the second paper of section A in which I argue that, contrary to his frequent claims, Bohr did not deduce the configurations of the elements from first principles. As others have also pointed out, he obtained these configurations by appeal to spectroscopic properties and chemical information on the elements. In this paper I also examine the specific case of the element hafnium, (Z = 72), whose electronic configuration according to all textbook accounts was predicted by Bohr. In fact, Popper on more than one occasion wrote that the prediction concerning hafnium and its subsequent discovery represents what he termed "the greatest moment in all the reductionist adventures of the twentieth century, superceded perhaps only by the breakthrough represented by Crick and Watson's discovery of the structure of DNA."[8] As I see it, Bohr used an essentially empirical argument to arrive at a configuration for hafnium that had previously been reached by chemists on purely empirical grounds.

In fact one can go even further back historically to examine whether, or the extent to which, the notion of electronic configurations originated with quantum theory. As the popular account has it, electronic configurations entered physics and chemistry when Bohr first introduced quantum theory into the study of atomic physics. This is perhaps a natural assumption given that there is a sense in which quantization of electron energy is synonymous with the notion of electrons in energy levels or shells. But, surprisingly perhaps, the idea of electrons in shells pre-dates Bohr's model of the atom and has no connection with quantum ideas of any form whatsoever.

Electronic configurations, although not so named, were first introduced in J.J. Thomson's purely classical model of electron rings within the positively charged atom or what is often called his plum pudding model. But the idea of assigning electrons to rings goes even further back to the experiments of American physicist Alfred Meyer.[9]

In the third paper of section A the reduction of chemistry to modern quantum mechanics is finally considered. As mentioned earlier, this is carried out by examining the degree to which approximate solutions of the Schrödinger equation, and other calculations that are afforded, can

predict the quantitative aspects of modern chemistry such as ground state energies, bond lengths, bond angles or the magnitude of dipole moments.

It must be emphasized straight away that such predictions are rather impressive. This is a situation that needs to be better appreciated by those philosophers who are too willing to declare that chemistry simply does not reduce to physics without bothering to enter into any details. The days when ab initio quantum mechanical calculations were only useful for systems of up to ten or twenty electrons are now long gone.

The approach taken in this paper is first to consider the reduction of the periodic system as it is taught to high school and undergraduate students and then to move on to the way the question is addressed by the professional theoretical chemist. In high school textbooks students are told that the periodic table can be explained very successfully by recognizing that the elements that fall in the same groups show analogous outer-shell electronic configurations. At a slightly higher level, say freshman chemistry, the explanation becomes more sophisticated and is given in terms of the possible values of the four quantum numbers that are associated with each electron in an atom.

What is not made clear is that while the quantum number approach can account for the maximum occupancy of each electron shell, it cannot predict the lengths of successive periods. But since this independent-electron approach is known to be an approximation professional chemists are not too dismayed by its inability to explain the periodic system exactly. What they might suggest, in this context, would be to examine the outcome of accurate calculations. Here the independent-electron approximation is taken as a starting point but all manner of corrections are added. Those in favor of reduction are more likely to pin their reductive aspirations on this kind of approach.

Not surprisingly it turns out that such an approach is far superior that the one that assumes a single fixed configuration for an atom, but the computational gap when compared with experimental energies is still not completely bridgeable. Ground state energies can be computed to increasingly accurate values but not completely theoretically. Calculated ground state energies can be made to tend ever closer to experimental values but only by taking the mathematical expansions to the limits of what modern computers are capable of. As yet there does not exist an

elegant 'once and for all' solution to explain the entire periodic system at once. Instead the Schrödinger equation for each atom must be solved separately. Finally I discuss an approach that began as a quite different method from the one based on wavefunctions and atomic orbitals. This alternative approach consists of the density functional method, which initially made no appeal whatsoever to atomic orbitals since it regarded electrons as a homogeneous gas. But modern developments within this technique have resulted in the blurring of the distinction between the wavefunction and density functional approaches. One typically carries out a density functional calculation but with the inclusion of experimental data on certain atoms. There is no completely ab initio density functional method that has been devised. And so much the worse therefore for the claims to a full reduction of the periodic system.

In the fourth paper I consider the ontological reduction of chemistry rather than epistemological reduction. As mentioned earlier, in this introduction, philosophers are not always persuaded by the naturalistic arguments that I presented in the previous paper. If present day quantum physics fails to fully reduce present day chemistry this may be due to some deficiencies in one or both of these enterprises. It may be due to our inability to bridge the computational gap effectively, even if the two descriptions are perfectly faithful in representing the fields of physics and chemistry. Many philosophers of a more analytical bent, who have not been persuaded by Quine's insistence that there is no 'first philosophy', are likely to ask whether there is any reason why chemistry is in principle not reducible to quantum physics.

Moreover there has been something of a return to metaphysics. This is because many philosophers consider that Kripke refutated Quine's position. This development has in turn reinforced the belief that one can do metaphysics without too much concern for the details of chemistry and physics of the kind that I favor.[10] In this arena I have been more of a critic than an immediate participant. My role has been confined to examining whether the metaphysical arguments do justice to the current scientific findings even if they are not directly derived from them. In the fourth paper of this section I therefore discuss the attempts by two contemporary philosophers, one a philosopher of mind and the other a metaphysician, to draw conclusions about the ontology of chemistry. The

first is by Brain McLaughlin and concerns his pronouncements on the role, or rather a lack of any role, as he sees it, for what is termed downward causation in chemistry. In a few words, downward causation is an anti-reductionist notion that supposes that matters of fact occurring at a macroscopic level are able to, as it were, reach down to the microscopic components of a system to influence its behavior. McLaughlin's paper examines some notions of downward causation that have been proposed by a number of emergentist philosophers and concludes that downward causation is out of the question. McLaughlin's basis for this conclusion is the success of the quantum mechanical theory of bonding, or at least his 'spin' on this theory.[11]

The second paper I consider is more explicitly ontological in that the author, Le Poidevin, attempts to discuss the ontological reduction of chemistry via a completely metaphysical approach which does not involve the findings of modern physics and chemistry in any way. Le Poidevin adopts what he calls a combinatorial approach in order to answer such questions as why Mendeleev regarded the missing gaps in his periodic system as actual physical possibilities rather than merely logical ones. My conclusion on both these papers is that the authors are mistaken. I claim that McLaughlin's argument against downward causation is insufficient and that Le Poidevin's defense of the ontological reduction of chemistry is inconsistent. This could be taken to mean that I support anti-reductionism and I suppose I do in a sense. However I will not delude the reader by pretending that I give any positive anti-reductionist arguments in this paper or that I provide arguments in favor of the emergence of chemical phenomena from physical ones. All I can really claim to have done in this paper is to have perhaps refuted the anti-reductionist arguments of two philosophers. Perhaps I have thereby left the door open to the possible existence of emergence and for the lack of reduction of the chemical to the physical.

Section B. Periodic Table, Electronic Configurations and the Elements

The papers in this section range across a number of related areas and the theme of reduction is still present as it has been in virtually all my work.

Very few papers have examined the philosophical nature of the periodic system, in spite of its huge importance in chemistry, physics and science generally. This is also surprising given that the periodic system provided strong early motivations for the ground-breaking work of a number of physicists like Thomson, Rydberg, Bohr and Pauli.

One of the exceptions is a paper by the Dutch philosophers Hettema and Kuipers which attempts to affect an axiomatization of the periodic table in the classic tradition of logical positivism or structuralism as one modern version is known. When I said earlier that the former logical approach to philosophy of science was redundant, I was of course exaggerating a little. Hettema and Kuipers attempt to axiomatize the periodic system and to thereby draw some philosophical conclusions regarding the status of the periodic system as well as the status of chemistry in general. Unfortunately the attempted axiomatization does not succeed because the manner in which the periodic table is portrayed seems to be rather problematic. For example the authors examine what they call the transition from Mendeleev's naïve periodic law to a sophisticated modern periodic law that is underwritten by quantum mechanics but the way that the naïve periodic table is characterized by them is patently incorrect as I have argued in my response. The authors claim that chemists and physicists have a different conception of the atom but as far as I can gather do not provide a convincing argument to that effect. And just to cite another of their claims, they propose that atomic theory can explain and even reduce the chemist's formulation of the sophisticated periodic table. As in the previous two cases I provide arguments to show that such a claim is untenable.

Still on the periodic table, the second paper examines attempts to explain the periodic system through electronic configurations of atoms. The decision to place this article in the present section is based on the fact that the question of reduction is being restricted to asking about the status of the periodic system rather than chemistry as a whole as in the case of the papers in section A. The article in question also provides an opportunity to consider different levels of explanation in chemistry. From a methodological point of view it involves an examination of the major kinds of approaches in computational quantum chemistry, namely the wavefunction and density functional approaches respectively.

Although the first of these approaches has been examined by a number of philosophers of science[12], I am not aware of anybody other than myself who has written about the nature of the more recent density functional approaches in the philosophical literature.

Whereas the philosophy of science has tended to concentrate on scientific theories as the basic unit to be scrutinized, the coming of a more naturalistic approach has produced much work on the nature and function of scientific models. The second paper in section B originally appeared as a contribution to a symposium on "paper tools" held at the Max Planck Institute for the History of Science held in Berlin in 1999. In this paper I try to examine the extent to which the periodic system, which I claim is a paper tool *par excellence*, may or may not be a typical scientific model.

In doing so I hope to uncover some previously unexamined aspects of the periodic system. The first concerns the question of why vertical relationships among elements, from the perspective of the modern table, were discovered well before any horizontal relationships. My suggestion is that any errors in obtaining correct atomic weights are consistent within a group of chemically similar elements since the elements generally share the same valence. However in moving horizontally across the periodic table the elements show variations in valence and so any method that did not recognize the role of valence in determining atomic weight would have produced an inconsistent ordering of elements. It was only later in the history of chemistry that it was realized that atomic weight is the product of valence and equivalent weight.

Secondly, I argue that an early system developed by Leopold Gmelin in 1843, although mentioned by some authors, has not been appreciated for its full worth. Briefly put, the system anticipates the grouping together of 19 main group elements as well as implicitly arranging the elements in order of increasing atomic weight.

Finally, the paper contains the beginning of a discussion which I have since developed in more recent articles, on the question of whether the representation of periodic system is a matter of convention or whether there is any sense in which the classification of the elements may be said to reflect objective matters of fact regarding which elements belong together in particular groups. In the paper reprinted here I still

agreed with the prevailing view that representation is a matter of convention, a point on which I have subsequently changed my mind as will become clear from the last paper reprinted in this section.

The other main theme in section B concerns the philosophical nature of the elements. An important aspect of the chemical revolution consisted in Lavoisier's emphasis on elements as substances that could actually be isolated and a turning away from regarding elements as unobservable bearers of properties. The fact that his suggestion has been enormously productive is of course completely undeniable as in the case of other positivist approaches in the scientific revolution in general.

However, the turning away from regarding the elements as unobservable abstract entities could not be sustained for long. The concept returned rather forcefully with Mendeleev's version of the periodic system of the elements. In fact Mendeleev repeatedly emphasized that in his classification of the elements, the emphasis was primarily on the unobservable sense of the concept of 'element'. In some instances Mendeleev even called them 'the real elements' and carefully distinguished this concept from elements as simple substances or Lavoisier's elements.

The next major resuscitation of Mendeleev's 'real elements' took place at a rather crucial historical juncture at which the rapid discovery of isotopes threatened to render the chemist's periodic table redundant. Some chemists pointed out that the number of 'elements' seemed to have grown out of all proportion and that it would necessitate moving to a table of isotopes. But as Austrian born Fritz Paneth recognized, this would have represented putting all emphasis on the elements as simple substances that could actually be isolated or, in other words, on the isotopes. If attention were placed on unobservable elements, in the manner recommended by Mendeleev, the chemist's periodic table could be salvaged. The only change required was to characterize these 'real elements' by their atomic number rather than by their atomic weights as Mendeleev had done.

The philosophical aspects of this episode are rather far reaching for the question of the reduction of chemistry. Paneth himself subsequently discussed the issue in depth in a highly influential article that first appeared in the British Journal for the Philosophy of Science.[13] Paneth's

take-home message is that the chemist need not slavishly follow every reductive step that is suggested by developments in physics. Since isotopes of the same element generally show identical chemical properties, what the chemist regards as an element need not be the same as that understood by the physicist. In more general terms, the reduction of chemistry although strictly applicable in some cases, may not always be beneficial to the chemist. In an article which has previously appeared in an edited collection on philosophy of chemistry, and which is reproduced in the present volume, I examine the background of the dual sense of the concept of 'element' and I discuss the general importance of this issue.

In a second paper on this theme, which is also included in this section, I try to go further in applying the notion of Mendeleev's 'real elements', called basic substances by Paneth, to a long-standing problem having to do with the periodic table. The conventional or medium-long form periodic table displays a number of periods of elements starting with an extremely short period of just two elements, hydrogen and helium. Unlike subsequent periods of 8, 18 and 32 elements that show repetitions, the extremely short period of two elements does not repeat. Many attempts have been made to remove this anomaly and to render the sequence of period lengths more regular. One such attempt goes by the name of the left-step periodic table that was first published by Charles Janet in the 1920s. Here the regularity in period length is achieved by placing helium in the alkaline earths. In order to justify such a chemically controversial move, some authors have appealed to the phenomenon of first member anomaly, according to which the first member of all groups in the periodic table show distinctly different properties from lower members. It is argued that the apparent difference between helium and the alkaline earths, in the left-step table, should be regarded as a more extreme case of first member anomaly, something akin to the difference between hydrogen and the alkali metals.

In the paper in this section I have suggested a philosophical way of accepting the placement of helium among the alkaline earths that does not depend of chemical or indeed physical properties. If one returns to the insistence on the 'real elements', then the chemical and physical differences between helium and the alkaline earths should be considered

as only reflecting the properties of the elements as simple substances which are consequently not of paramount importance in establishing an optimal classification of the elements. But more recently I have revised this view and have argued that it is hydrogen rather than helium that should be relocated. In doing so I relocate hydrogen at the top of the halogen group on the grounds that one thereby gains a new perfect atomic number triad.[14]

Section C. Realism and Anti-Realism, and Educational Issues in Philosophy of Chemistry

As mentioned in the brief biographical section above, my main motivation that led me to the philosophy of chemistry was the practice of chemical education. I have repeatedly suggested that modern chemical education lacks philosophical depth. I have also urged that a more philosophical examination of the subject matter in general chemistry courses is the single most important step that can invigorate the teaching of chemistry.

I believe that some influential researchers in the field of chemical education have taken a rather shallow approach to the study of philosophy of science. They enjoy quoting authors like Kuhn because they have been led to believe that the only sensible approach to science education lies in adopting 'constructivism'. Rank and file educators are constantly berated for taking what these researchers call a positivist approach. Because they read in popular accounts that logical positivism is an outdated philosophical approach they embrace the opposite extreme philosophy. They do so, I claim, without taking the trouble to examine the evolution from logical positivism to Popper, through Kuhn and Lakatos to the frankly outlandish relativism of Feyerabend and some other contemporary relativists.

The chemical education profession is dominated by chemical constructivists who take as their role model the chemist-educator Dudley Herron. In an earlier paper, which made me rather unpopular in these circles, I undertook a critique of the views of Herron and some of his contemporary followers like Bodner and Spencer. Although I have received numerous favorable comments from educators who are frustrated with the predominance of constructivist views, the protagonists

subsequently published an article in the *Journal of Chemical Education* because of the educational importance of this issue. Had the Arizona authors been correct, all chemistry and physics textbooks would have been in need of serious modification but no such changes have been made.

I then wrote another article on this subject, which appeared in the *Proceedings of the Philosophy of Science (PSA)* meeting for 2002 and which was intended for a more philosophical audience. I think the questions raised by this episode are interesting philosophically because they touch on the nature of observation, the nature of theoretical entities and the question of the reference of scientific terms. I believe the issue is also relevant to the question of scientific realism. There has been a good deal of interest in the question of whether scientific terms refer or not. Larry Laudan has published an influential paper in which he points pout that many now defunct scientific theories, which were at one time successful, featured scientific terms which in hindsight could not have been genuinely referring. For example, the terms caloric, phlogiston and ether all featured prominently in theories of heat, chemistry and electrodynamics respectively but they all turned out to be redundant entities. Laudan's conclusion is that the success of scientific theories does not give us grounds for treating their central scientific terms as real in the sense of being genuinely referring to objective entities in the world.

But Laudan stops short of examining theoretical terms used in currently viable scientific theories. In the case of atomic orbitals we know that the scientific term does not refer even though the theory, quantum mechanics, remains viable at present. I therefore offered the example of atomic orbitals in my article as a means of strengthening Laudan's case by encompassing current theories. But it now occurs to me now that rather than supporting his case, I may actually be undermining it. The decision to call a scientific term non-referring does not require that the theory should have been refuted as Laudan seems to imply. The relationship between reference and the status of a theory seems to be weaker than Laudan supposes. Atomic orbitals provide a case in point. They are extremely useful in calculations in chemistry and physics and yet are known to be non-referring. Whether or not quantum mechanics is

eventually refuted will not be the basis for deciding whether orbitals refer or not. We already know that they do not. This incidentally is what makes the Arizona State claim all the more puzzling, as was the unflinching support which these authors seemed to enjoy from the editors of *Nature* magazine who refused to publish letters objecting to the claims.

The final paper in the collection, rather appropriately perhaps, is somewhat retrospective and first appeared in 2006 in a volume of the *Boston Studies in the Philosophy of Science*. In it I begin by reviewing some history of philosophy as far as it concerns the swing from psychologism to the anti-psychologism as advocated by Frege. I then move to a discussion of the more recent tendency, begun by Quine to move away from normative philosophy towards a naturalistic approach. I proceed to examine my own work in the light of philosophical naturalism since it has been one of my main motivations in examining what aspects of chemistry can be derived from quantum mechanics.

I then engage in an examination of the interaction between normative and descriptive aspects in my research in the philosophy of chemistry and suggest that what began as normative work on the nature of atomic orbitals, for example, eventually turned into descriptive work. That is I concede that chemists use orbitals in a manner that is distinct from that of physicists and furthermore that they are fully entitled to do so in the light of the degree of autonomy which chemistry enjoys from fundamental physics.

Conversely I believe that some other aspects of my work have involved a movement in the opposite direction, namely from an initially naturalistic emphasis towards making normative recommendations. This is the case in the work that I have carried out in examining the details of attempts to reduce chemical quantities to physics via quantum mechanical calculations based mainly on the Schrödinger equation. However based on such examinations I believe I have drawn normative conclusions to the effect that researchers in quantum chemistry might consider being clearer about just how much is strictly derived in an ab initio manner when performing what they typically term "ab initio quantum chemistry". Or to return to the title of an earlier paper in this

volume, it has allowed me to ask the question of "just how ab initio is ab initio quantum chemistry?".

Finally I hope that this volume will stimulate further work in the burgeoning field of the philosophy of chemistry and that my views will be subjected to careful scrutiny by members of the philosophy of chemistry community as well as chemical educators, chemical historians, chemists physicists and practicing quantum chemists.

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[2] J. van Brakel, On the Neglect of the Philosophy of Chemistry, *Foundations of Chemistry*, 1, 111-174, 1999.

[3] For example there is nothing in this volume on the question of chemical synthesis, or smell or organic chemistry.

[4] This is not to say that such activities have ceased altogether. For example Hettema and Kuipers have attempted to axiomatize the periodic table of the elements and continue to defend their attempt to do so.

[5] If one takes the Quinean approach then perhaps I have been examining the ontological reduction of chemistry all along in my own work, since I have examined the details of chemical and physical theories.

[6] A special issue of the journal *Synthese* edited by Lee McIntyre appeared to celebrate the 10th anniversary of the foundation of philosophy of chemistry which actually took place in 2004. L. McIntyre, The Philosophy of Chemistry: Ten Years Later, *Synthese*, 155, 291-292, 2006.

[7] O. Lombardi, M Labarca, The Ontological Autonomy of the Chemical World, *Foundations of Chemistry*, 7, 125-148, 2005.

[8] I had the pleasure of discussing this issue personally with Popper in 1994 and, I believe, in convincing him that he was mistaken in this claim.

[9] I do not examine the pre-quantum mechanical origins of electronic configurations in this book but have done so elsewhere. E.R. Scerri, *The Periodic Table: Its Story and Its Significance*, Oxford University Press, 2007. See chapters 7 and 8 especially.

[10] J. Fodor, Water's Water Everywhere, Review of Christopher Hughes', Kripke: Names, Necessity and Identity, *London Review of Books*, 21st October, 2004. or
http://www.lrb.co.uk/v26/n20/fodo01_.html

[11] As the reader will note, this case is somewhat intermediate in terms of epistemological and ontological reduction as I have defined them here. It may be described as ontological in the sense that it deals with issues of causation and in particular downward causation. However what McLaughlin appeals to as the final arbiter are the details of current theories, namely the quantum theory of chemical bonding, which is surely an epistemological issue.

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[14] E.R. Scerri, The Past and Future of the Periodic Table, *American Scientist*, 96, January-February, 52-59, 2008.

[15] At the time of compiling this book of collected papers a brief response from Herron had finally appeared. J.D. Herron, Advice to My Intellectual Children, *Journal of Chemical Education*, 85, 24-32, 208.

Section A

Philosophy of Chemistry and the Question of Reduction

themselves have maintained a deathly silence, at least in the literature.[15] Not thinking it possible that I might have killed off the entire field I recently returned to the publications of Bodner and some others.

It appears that the former outright foolishness of arguing in favor of relativism has been abandoned. And I can only hope that my critique contributed in some small way to this change. However, the recent work remains philosophically problematic even if not quite so glaringly as in the late 1990's. For example, in a co-authored article of 2006 Bodner et al argue that Popper was a positivist. They go to great lengths to interview all manner of students and experts in chemistry to reach the apparently startling conclusion that chemists do not generally speak in terms of laws and attempts to refute laws. Bodner and colleagues seem to be blissfully unaware of the fact that Popper was the first and most influential critic of positivism and that his work contributed to the downfall of Logical Positivism.

The paper in section C that is reprinted here was written after the one that appeared in the *Journal of Chemical Education*. Because this later paper was directed at an audience of philosophers I chose to begin by reviewing the Science Wars and the Sokal affair. I emphasized that in most cases the opponents of the 'academic left' tend to be scientists who abhor relativism. This makes it all the more surprising that some chemical educators, among the constructivists, have been willing to support a relativist position concerning scientific knowledge. One cannot help wondering how much of this confusion among the chemical education community is the result of an absence, until recently, of any literature on the philosophy of chemistry.

In 1999 a rather sensational development was announced on the front page of *Nature* magazine. At least it would have been sensational if it had turned out to be true. Some chemists and physicists at Arizona State University claimed that they had obtained observations of atomic orbitals. As somebody who had done some work on the nature and philosophical status of atomic orbitals I immediately sent a letter to the editors of the journal to point out that orbitals are not observable as a matter of principle and that something had to be wrong with the Arizona State claim. The letter was not published, and nor were several other letters which also tried to protest about the impossibility of such claims. I

ERIC R. SCERRI and LEE McINTYRE

THE CASE FOR THE PHILOSOPHY OF CHEMISTRY

ABSTRACT. The philosophy of chemistry has been sadly neglected by most contempory literature in the philosophy of science. This paper argues that this neglect has been unfortunate and that there is much to be learned from paying greater philosophical attention to the set of issues defined by the philosophy of chemistry. The potential contribution of this field to such current topics as reduction, laws, explanation, and supervenience is explored, as are possible applications of insights gained by such study to the philosophy of mind and the philosophy of social science.

1. INTRODUCTION

Even a cursory review of contemporary literature in the philosophy of science reveals an interesting fact: while there are separate sub-disciplines for "the philosophy of physics" and "the philosophy of biology", there is one foundational science that is missing. Why has there been no philosophy of chemistry?

Of course there has been a small literature dealing with some special philosophical problems in chemistry, sometimes even yielding an article with "philosophy of chemistry" in its title. Indeed, recently the field has seen both a special issue of *Synthese*[1] (1986) devoted to a symposium on "The Philosophy of Chemistry", and a symposium held at the biennial meeting of the Philosophy of Science Association (1994) on "The Philosophy of Chemistry".[2]

But while the *quality* of the literature that has appeared so far has been very high, the *quantity* is out of all proportion to that of the philosophy of physics and the philosophy of biology, and what *has* appeared has not yet convinced most philosophers of science of the legitimacy of chemistry as an area of philosophical concern. That is, even if one wishes to argue the point of whether there does already exist a small sub-discipline of the philosophy of science called "The Philosophy of Chemistry", even its practitioners must admit that it is still in its infancy, or at least that it is "pre-paradigmatic". And, perhaps most obvious, the philosophical literature on *any* aspect of chemistry is *extremely* sparse, especially when considering that physics, chemistry, and biology are the dominant triumvirate in the

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natural sciences. One must conclude that the set of issues one would naturally associate with a "Philosophy of Chemistry" has at least been radically ignored.

But why? Is it that there is nothing interesting for philosophers to *say* about chemistry as a scientific discipline? Is chemistry in and of itself perhaps less fruitful as a source of interest for the traditional concerns of philosophers of science? Or is it, more likely, the prejudice that given chemistry's unique relationship to physics, every interesting *philosophical* issue that might arise as a result of studying chemistry is merely an artifact of some *more* interesting on-going area of concern within the philosophy of physics?[3] That is, just as it is widely believed that chemistry can be perfectly reduced to physics, so perhaps it is believed that the philosophy of chemistry can be perfectly reduced to the philosophy of physics.

But even if one did happen to believe that all of the interesting facts about chemistry as a philosophical subject were eclipsed by the concerns of the philosophy of physics, such a position would need to be motivated. That is, one would need to feel confident that the sources of possible philosophical concern within chemistry had at least been *identified* by philosophers of physics, then to show that they could be happily abandoned as a result of the foundational level at which such issues were already being dealt with by philosophers of physics. One does not, however, gain such confidence in looking at contemporary literature in the philosophy of science. Indeed, far from looking to other fields like chemistry for philosophical fodder, until the relatively recent appearance of the philosophy of biology, the philosophy of science itself was dominated by the philosophy of physics, which in turns appears to be practically exhausted by quantum mechanics, relativity, and space-time (Hull 1979, Cartwright 1979).

Given the unique placement of chemistry *between* physics and biology in the traditional hierarchy of the natural sciences, however, isn't it reasonable to assume that chemistry may yield a set of issues worthy of increased philosophical attention? Indeed, one might point out that chemistry has traditionally been, and continues to be, the science concerned with the nature of the elements, of substance and indeed of the nature of matter, again all traditional philosophical questions. We should not be too misled by the fact that the study of matter, during the twentieth century, seems to have slipped out of the hands of chemists and into those of theoretical physicists. Falling into such a trap would be doubly erroneous, since physics has only usurped chemistry when it comes to the micro-structure of matter and secondly because it would be question begging over the issue of the reduction of chemistry, which we claim is the one of the main areas in which philosophical interest in chemistry should be directed. And,

even if one is convinced that chemistry ultimately is reducible to physics, chemistry itself has not withered away. Why so, then, the philosophy of chemistry?

In this paper, we will argue that the Philosophy of Chemistry is an important area of study within the philosophy of science in its own right, and we will seek to identify some chemical issues which we believe worthy of increased philosophical attention. Moreover, we will argue that the insights gained through studying the philosophy of chemistry may pay dividends for more traditional debates within the philosophy of the special sciences. At the end of this volume, we have also offered a comprehensive bibliography of works that have appeared so far, which might be grouped under the heading "Philosophy of Chemistry", in the hope that philosophical debate will be furthered by knowing what has already been done.

2. REDUCTIONISM

Perhaps the most appropriate place to begin our analysis is with the issue of reductionism, due to the unique ontological relationship that exists between chemistry and physics. Indeed, it is the closeness of this relationship that has probably led many philosophers of science to assume that the reduction of chemistry to physics is both trivial and inevitable. But does chemistry provide such a paradigm case for reductionism? And, if so, why have so many chemists (and even physicists) been reluctant to eclipse the concerns of chemistry with those of physics? Or, does the relationship between chemistry and physics instead highlight a case where despite ontological dependency, we wish to preserve the epistemological and explanatory autonomy of our original subject?

Of course, we must here begin by stating what we mean by the blanket term "reduction", and what we take to be some of the problems it faces.[4] First of all, we will not be primarily concerned with the ontological dependence of chemistry upon physics. As stated, we believe the ontological dependence of chemistry on physics to be almost a foregone conclusion. Rather, our concern will be with the epistemological reduction of chemistry to physics – with the question of whether our current description of chemistry can be reduced to our most fundamental current description of physics, namely quantum mechanics – and with its explanatory consequences.[5]

The debate over reduction has had a long and storied history within the philosophy of science, and there is continuing debate over the adequacy of different accounts of it.[6] The classic, and still widely embraced, view of reductionism has been given by Ernest Nagel, in his book *The Struc-*

ture of Science.[7] Nagel-form reduction involves the axiomatization of both theories in question and an examination of whether certain formal relationships exist between the axiomatized versions of these theories. First of all, it is not clear that the laws of chemistry, if indeed they exist, (a topic to be discussed later) can be axiomatized. Secondly, even in cases where axiomatization of the two theories at issue has been affected it is not clear that the formal condition for a successful reduction have ever been met successfully. In other words, it is not clear whether any reductions at all of the Nagel form have ever been identified. However, these facts have not prevented some philosophers from simply asserting that chemistry does reduce to physics (Kemeney and Oppenheim 1956).

In addition to Nagel's account, there exist a plethora of other ways in which the term reduction has been discussed in the philosophical literature. Rather than here rehearsing these discussions on what one might mean by reduction, we now wish to concentrate on a form of reduction which has been discussed previously by one of us (Scerri 1994). We claim that this may be one of the ways in which thinking about chemistry may help to clarify issues in the philosophy of science and henceforth we shall focus on a more naturalistic approach to reduction, which may be described under the label of quantitative reduction.

Now, what might a chemist say about the reduction of chemistry? If one were to ask a contemporary chemist whether chemistry could be reduced to physics, he or she would probably direct us to a colleague in computational quantum chemistry, since these are the specialists who deal with such issues. A cursory examination of this branch of theoretical chemistry shows it to be an attempt to calculate the properties of atoms and molecules (including their reactivities) from first principles. This task is carried out via the Schrödinger equation, which may be described as the main workhorse of applied quantum mechanics. It should be said that there are many other pursuits in theoretical and physical chemistry which also broadly speaking fall under the umbrella of attempts to reduce chemistry. These other areas would include so called semi-empirical calculations in which certain experimental data are "fed in by hand" as it were. In such cases the philosopher will immediately object (with full justification) that such an approach, even if it were successful, would not constitute a genuine reduction, since one would be using not merely the reducing theory of quantum mechanics, but also some ingredients which belong to the science to be reduced, namely chemical data.

Thus, in order to be as even handed as possible, and to give the supposed reduction of chemistry the best chance of success, one would need to examine the research in the area of *ab initio* calculations, in which no

experimental data whatsoever are admitted into the computations.[8] The aim here is simply to calculate the energy of a molecule, a bond angle, a dipole moment, or a rate of reaction from the first principles of quantum mechanics.[9] How does this enterprise fare in contemporary chemistry?

We believe that even given this rather extreme perspective on the reduction of chemistry, the situation is one of an incomplete reduction. In one sense the failure of this reduction is very easily realized once one considers that the application of the Schrödinger equation even to a system as simple as the helium atom lands us directly at the door of the many-body problem. Solutions to the many-body problem are necessarily approximate, as is well known in physics. The sad fact for chemistry, moreover, is that only the Schrödinger equation for the hydrogen atom possesses an exact solution. This system is hardly of interest to "real chemists", whose concerns range over the remaining hundred or so elements in the periodic table. And even if one were to restrict attention to the element hydrogen, chemists are more frequently concerned with diatomic hydrogen (H_2) rather than the highly reactive hydrogen atom which is the only system to have been truly captured by quantum mechanics.

Nonetheless, leaving aside the inevitability of approximations in chemistry, we might still want to inquire as to how good the approximations actually are. This question should be approached rather carefully, and we suggest that a critical attitude should be adopted towards the claims made by the practitioners in the field. The source of latitude exercised by computational quantum chemists lies in a particular technical aspect which underlies much of the computational work. The approximations used in computational quantum chemistry involve the expansion of wavefunctions as infinite series of terms in much the same way as Fourier analysis seeks to represent a complex function as an infinite series of separate terms. The simple fact of the matter is that one may model a complex function to virtually any degree of precision, provided one is prepared to introduce an increasing number of correction terms in the series expansion. By adding greater flexibility to the wavefunction, something which can always be justified on a *post hoc* basis, one can obtain increasingly better approximations to the experimentally observed data which one is trying to calculate.

Admittedly, there is considerable virtue in demonstrating that a particular calculation works well in a certain test case, and then adopting the same approach to an unknown experimental situation. However, such an approach, referred to as the "calibrated *ab initio* method" may be justly criticized by the purist on much the same grounds as we discussed earlier in the case of semi-empirical calculations.[10] Both procedures involve the

importation of data from the level of facts to be reduced into the reducing theory.

There are measures which can be taken to estimate the goodness of the calculation independently of the experimental data and which thus lend the calculation greater reliability, but these are notoriously difficult procedures, and many computational quantum chemists become irritated at the very mention of such internal procedural checks.[11]

Essentially, these internal estimates consist in the determination of both upper and lower bounds in the calculation of any particular property such as the energy of a molecule. The problem arises because whereas the variation method, which lies at the heart of most approximations, can provide an estimate of the upper bound to the energy, the systematic calculation of the lower bound is still an open problem in quantum chemistry.[12]

Thus, we see from our example of the explanation, or more correctly the calculation, of chemical facts from first principles, that there are many difficulties for the reductionist view, which face the computational chemist. Of course, chemistry is concerned with a far broader range of explanations than those exhausted simply by calculating a certain property such as a dipole moment or a bond angle. To rest contented with only this notion of reduction in chemistry would surely be to adopt a rather narrow stance on what constitutes epistemological reduction. Still, the difficulties of the kind mentioned above reveal the weakness of an explanatory approach which overestimates the ease with which chemical phenomena can be perfectly captured and explained by theoretical notions drawn from physics.

We have concluded that quantitative reduction, the most overt attempt at reduction in chemistry, has not been achieved. However, we also note that the present failure to obtain simultaneous upper and lower bounds to *ab initio* calculations may eventually be overcome. If this problem were ever to be solved it would be possible to speak of approximate reduction of quantitative properties which are important in chemistry, such as the energies of molecules or bond angles. Full reduction would nevertheless remain unattainable since, as mentioned above, the Schrödinger equation only possesses an exact solution in the case of the hydrogen atom.[13]

However, we wish to carefully distinguish between the above form of "quantitative reduction"[14] of chemistry and what might be termed "conceptual reduction".[15] Such a distinction already has been made in the philosophy of chemistry, though perhaps somewhat obliquely, by Hans Primas, the author of the only book on the reduction of chemistry:

> Many calculations have been extremely sophisticated, designed by some of the foremost researchers in this field to extract the maximum amount of insight from quantum theory. For simple molecules, outstanding agreement between calculated and measured data has been obtained. Yet, the concept of a chemical bond could not be found anywhere in these

calculations. We can calculate bonding energies without ever knowing what a bond is! (Primas 1983).

It is conceptual reduction which is of greater relevance for the remainder of the present article. By conceptual reduction we mean attempts to reduce chemical concepts such as composition, bonding, and molecular structure.[16] In these cases we are not obliged to adopt an agnostic approach due to the present state of science. Rather, our claim is that this form of reduction is not even possible in principle due to the very nature of the concepts themselves. That is, the concepts of composition, bonding, and molecular structure cannot be expressed except at the chemical level.

Mario Bunge, for example, has made the point that the concept of chemical composition cannot be reduced to physics. Bunge writes,

> At first sight chemistry is included in physics because chemical systems would seem to constitute a special class of physical systems. But this impression is mistaken, for what is physical about a chemical systems is its components rather than the system itself, which possesses emergent (though explainable) properties in addition to physical properties. (Bunge 1982)

Bunge cites as an example of such an emergent property that of having a composition that changes lawfully in the course of time. The atomic and molecular components do not show this property of composition. Primas, as quoted earlier, says that we can calculate certain molecular properties, but we cannot point to something in the mathematical expressions which can be identified with bonding. The concept of chemical bonding seems to be lost in the process of reduction (Primas 1983).

Woolley, to cite another example, has raised a great deal of interest in saying that chemical structure cannot be found in the pure quantum mechanical formalism applied to a chemical system. Structure, he tells us, is imposed by using the Born–Oppenheimer approximation (Woolley 1978). One can do calculations which do not draw on the Born–Oppenheimer approximation, and not only do we obtain solutions but in some cases, such as molecular beam experiments, we can do more accurate calculations by omitting the Born–Oppenheimer approximation altogether. According to Woolley, the concept of molecular structure is absent at the quantum mechanical level.[17]

In each of the cases cited, as well as others, we encounter chemical concepts that seem irreducible. Thus, even where chemical relationships may at base be dependent upon physical ones, it nonetheless seems perfectly appropriate to reject reductive *explanations* in some instances, where the concepts we employ and even the very explanandum itself may be lost in the theoretical terms of the primary science. That is, we may admit

the ontological dependence of chemical facts upon physical ones, and yet eschew the epistemological reduction of chemistry to physics.

3. EXPLANATION

Another potential area of interest in the philosophy of chemistry, closely related to the concerns of reductionism, would seem to lie in the investigation into the nature of chemical explanations. What do explanations in contemporary chemistry consist in? Are they "autonomous" from the concerns of physics? In what way?

At first brush, one may think that the close ontological relationship between chemistry and physics would inevitably bias chemical explanation in favor of reductionism. We shall see, however, that there is good reason to support the autonomy of chemical explanations. That is, even if we admit that chemical regularities are instantiated in physical relationships, it may be most useful, perhaps, to describe and explain them at the chemical (secondary) level of inquiry.

One very important form of explanation which pervades all areas of chemistry, from teaching to frontier research, lies in talk of electron shells or orbitals, as they are often called. The formation of bonds, acid-base behavior, redox chemistry, photochemistry, reactivity studies, etc., are all regularly discussed by reference to the interchange of electrons between various kinds of orbitals.

This approach may at first sight seem to speak in favor of the epistemological reduction of chemistry to physics, since talk of electron shells is thought to belong primarily to the level of atomic physics. However, a more critical examination of the issues involved reveals no such underpinning from fundamental physics. It emerges that explanations in terms of electron orbitals, and indeed all talk of orbitals in chemistry, is not sanctioned by our present understanding of quantum mechanics. The remarkable fact is that at the most fundamental quantum mechanical level electronic orbitals become ontologically redundant. Electronic orbitals simply do not exist according to quantum mechanics, although they remain as a very useful explanatory device. This result is embodied in the more fundamental version of the Pauli Exclusion Principle, which is frequently forgotten at the expense of the restricted and strictly invalid version of the Principle, which does uphold the notion of electronic orbitals (Scerri 1991, 1995).

This situation implies that most explanations given in chemistry which rely on the existence of electrons in particular orbitals are in fact "level specific" explanations, which cannot be reduced to or underwritten by quantum mechanics.[18] Thus, a case has been demonstrated where the

explanation of what it is that we seek to know when we engage in chemical explanation would seem to suggest that we eschew reductive explanations, and support the explanatory autonomy of chemistry.

4. LAWS

Just as there are some typically chemical explanations, such as talk of electron orbitals, which are best pursued at an autonomous level of explanation, we now suggest that there are also some irreducibly chemical laws as well. A good example of such a chemical law is provided by the so called periodic law, as first discovered by Mendeleev and Meyer, but anticipated by many others.[19] Viewed from the perspective of physics, the status of the periodic system may appear to be far from law-like. Significantly, the periodic law seems not to be exact in the same sense as are laws of physics, for instance Newton's laws of motion. Loosely expressed, the periodic law states that there exists a periodicity in the properties of the elements governed by certain intervals within their sequence arranged according to their atomic numbers.[20] The crucial feature which distinguishes this form of periodicity from that found in physics is that chemical periodicity is approximate. For example, the elements sodium and potassium represent a repetition of the element lithium, which lies at the head of group I of the periodic table, but these three elements are in no sense identical. Indeed, a vast amount of chemical knowledge is gathered by studying patterns of variation which occur within vertical columns or groups in the periodic table.

Predictions which are made from the so called "periodic law" do not follow deductively from a theory in the same way in which idealized predictions flow almost inevitably from physical laws, together with the assumption of certain initial conditions. So, can the case be made that the periodic law should legitimately be considered a law of chemistry, and, moreover, that it is explanatorily irreducible? We shall argue that it can.

The historical facts surrounding the classic predictions of a number of unknown elements made by Mendeleev show that he used a vast store of chemical intuition, rather than a straightforward algorithm as a physicist might, when operating with a physical law. A clearer appreciation of the nature of the periodic "law" can be gained by considering how Mendeleev arrived at the specific details of his predictions on the elements gallium, germanium and scandium. Mendeleev himself gives a clear and unambiguous indication of his method in his textbook *The Principles of Chemistry*. The method consists of simultaneous interpolation within groups or columns as well as within periods or rows of the periodic table. This procedure is

achieved very simply by taking the average of the sum of the values of the four elements flanking the element in question. According to Mendeleev,

> If in a certain group there occur elements, R_1, R_2, R_3, and if in that series which contains one of the elements, for instance R_2, an element Q_2, precedes it and an element T_2 succeeds it, then the properties of R_2 are determined by the mean of the properties of R_1, R_3, Q_2 and T_2. (Mendeleev 1905)

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly gives the example of calculating the atomic weight of the element selenium, a property which was known at the time and which could thus be used to test the reliability of his method.

However, if one attempts to apply this method to the prediction of atomic weights, atomic volumes, densities and other properties of gallium, germanium and scandium one arrives at values which differ significantly from Mendeleev's published predictions. It should also be noted that Mendeleev's published predictions were generally remarkably accurate when compared with the properties of the subsequently discovered elements. This suggests great chemical intuition on the part of Mendeleev which allowed him to make minor modifications from his stated method whenever it was necessary. Mendeleev appears to be deviating from his professed approach, but nowhere does he deem it necessary to specify how and why he departs from the simple method of interpolation. This is one of the many examples which illustrate the approximate nature of his periodic law.

Nevertheless, Mendeleev considered the periodic law as sufficiently law-like in that it could not tolerate any exceptions, such as any deviation from the ordering of the elements according to atomic weight. In the case of the elements tellurium and iodine, for example, he predicted that the atomic weights of these two elements were in error since the available values suggested the opposite order to the one dictated by chemical properties. More specifically, tellurium showed a higher atomic weight according to the then measured values and an ordering of the elements based on this feature would have placed tellurium in the same chemical group as fluorine, chlorine, and bromine, where it did not belong in chemical terms. As it turned out, Mendeleev was correct to reverse the ordering but for the wrong reason. The atomic weights had in fact been approximately correct, but the ordering of the elements is better achieved by means of the atomic number of each element. This improved ordering scheme resulted from the work of Moseley in 1912, and its virtue lies in overriding any complications due to the isotopic mixture which occurs in most chemical elements.

Mendeleev had sufficient confidence in his periodic law to use it to predict the existence of several new elements, and the properties of their compounds, in addition to correcting the atomic weights of some already known elements. Nevertheless, this predictive aspect seems to have been overemphasized by historians of chemistry and writers of chemistry books. It appears that Mendeleev's ability to accommodate the already known elements may have contributed as much to the acceptance of the periodic system as did his dramatic predictions. For example, the citation which accompanies his being awarded the Davy Medal by the Royal Society of London makes no mention whatsoever of his predictions[21] (Scerri 1996).

Indeed, the major reason why it is Mendeleev above all others who is credited with discovering chemical periodicity is that he elevated the periodic law to the status of a law of nature, and spent the remainder of his life in boldly examining its consequences and defending its validity. Nor was this a simple task since the periodic system was frequently challenged by subsequent discoveries of new elements. For example, in 1913 Ramsey and Rayleigh discovered the element argon, followed by a number of other noble gases. The name of these elements derives from their extreme reluctance to enter into chemical combination with other elements, a fact which led some chemists to suggest that they did not even belong in the periodic table. The noble gas elements had not been predicted by Mendeleev or anybody else and it required five years of intense effort by chemists and physicists before they were eventually successfully accommodated into the table. This was done in the form of a completely new column situated between the halogens and the alkali metals.

To sum up, we have argued that the periodic law is regarded as highly law-like in chemistry and that there exist no exceptions to it. Yet, the nature of the law is such that it cannot be captured by a simple numerical relationship,[22] and the regularity it captures cannot be expressed in nomological fashion using non-chemical concepts. The law expresses an approximate trend among the properties of the elements and their compounds. But if one attempts to express this trend numerically, such a relationship is found to hold only approximately. The periodic law thus stands as an autonomous law of chemistry. We disagree with Hettema and Kuipers who claim that the periodic table has been reduced to "atomic theory"[23] (Hettema and Kuipers 1988). This erroneous claim is based on the fact that elements within any one group tend to share the same outer shell configuration. However there are numerous exceptions to this model and the possession of a particular configuration is neither necessary nor sufficient for inclusion of an element in any particular group of the table. The reduction of the periodic table should in our view mean the ability to

calculate exactly the total energies or other properties of the atoms in the periodic table. Such a reduction is at best approximate as it is subject to the usual limitations of solving the many-body Schrödinger equation.

5. SUPERVENIENCE

The notion of supervenience has been much discussed in recent years throughout the philosophy of science.[24] Indeed, some authors have even drawn on the relationship between chemistry and physics to illustrate their basic arguments about the supervenience relationship (Papineau 1993). In doing so, however, it has been assumed that the relationship between chemistry and physics does not raise any particular problems of its own. Thus, as in many discussions of the appropriateness of chemistry and physics as an example of pure reduction, the relationship between chemistry and physics has been taken by some to represent a paradigmatic case of true supervenience. But is this move warranted?

Although there is notoriously no unanimous agreement on what the supervenience relationship is, the most popular view is that supervenience is a relationship of asymmetric dependence. Two macroscopic systems which have been constructed from identical microscopic components are assumed to show identical macroscopic properties, whereas the observation of identical macroscopic properties in any two systems need not necessarily imply identity at the microscopic level. In simpler terms, the phenomena we study in some secondary science are thought to be ontologically dependent upon relationships at the primary level. This argument has been widely used throughout the philosophy of science (and the philosophy of mind) as a rescuing maneuver from the impasse produced by the failure to establish the epistemological reducibility of any of the special sciences. Why? For the simple reason that supervenience is taken to make no guarantee about the epistemological or explanatory consequences which would necessarily follow from even a strong ontological dependence between two different descriptive levels.[25] Thus, the claim has been that supervenience allows us the virtue of ontological dependence, without the vice of explanatory reduction – it allows us to "have our cake and eat it too", as the saying goes.

Thus, although reductionism may fail in the traditional sense (that is, although there may be a breakdown in our efforts to establish a seamless continuity between the special sciences and quantum mechanics), we yet can maintain that, deep down, chemical or biological systems are governed solely by physical laws. Materialism is rescued, even though reduction has been found to flounder. Moreover, we need not appeal to "ontological

emergence", the "supernatural", or other questionable notions in order to get our epistemological autonomy.

Some authors, however, have suggested that this attempt to rescue explanatory autonomy from the jaws of ontological dependence is nothing more than a sleight of hand. As Paul Teller asks in the title of his paper, "Is Supervenience Just Disguised Reduction?"[26] Leaving aside the fascinating questions raised by this more general debate, we believe it is here interesting to examine the appropriateness of the use of the relationship between chemistry and physics to demonstrate the supervenience relationship.

6. DOES CHEMISTRY SUPERVENE ON PHYSICS?

In considering an answer to our above question, we shall consider the property of "smell" in order to examine more specifically what the supervenience of chemistry on physics might entail. According to the general supervenience argument which was outlined above, we take it that if two chemical compounds were "constructed" out of elementary particles in an identical manner, they would share the same smell (among their macroscopic properties). This is a philosophical claim which could be examined with respect to what is known empirically about the chemistry of smell. Similarly, the supervenience argument would entail that if two compounds share the same macroscopic property of smell, we could not necessarily infer that the microscopic components from which the compounds are formed would be identical. In the following, we do not propose to give an analysis of the state of the art in the chemistry of smell, but will restrict ourselves to a few general philosophical remarks, which highlight the relevance of considering such an issue as a legitimate one for the Philosophy of Chemistry.

It would appear that two opposing possibilities present themselves:

(A) Why is it that we are prepared to accept the notion that two compounds which have the same smell do not have an identical microstructure? Could it be because the property of smell is a rather vague concept, which does not seem susceptible to quantification? However, smell is indeed an explanatory concept in chemistry, and in keeping with our previous remarks about chemical explanations, such explanations cannot be reduced without remainder to physics, as compared to some other chemical data which do seem susceptible to approximate reduction.

On the other hand, if smell were rendered quantitative by some future advances, then we might be justified in insisting that two substances sharing the same numerical data regarding their degree of smell *should* share exactly the same microstructure. In other words, we *would* expect a reduction of

the smell-like data just as it is reasonable to expect an approximate reduction of the energy of a molecule. Were it possible to reduce these aspects of the chemistry of smell, then the claimed asymmetry in the supervenience argument would have been falsified in this case.

(B) The following intuition about the property of smell would seem to lead to the opposite conclusion, in that one would want to uphold the general spirit of what it means for smell to supervene over the physical make-up of a compound, and more specifically to uphold the claimed asymmetry.

Smell is a rather curious property in that its perception is thought to arise from a lock-and-key mechanism, whereby a certain molecular shape will trigger a particular smell receptor, and thus produce the sensation of a particular odor. Seen in this way, it would seem that two vastly different molecules which share the same molecular side-chain (which is required to trigger a certain smell receptor) would do so irrespective of the structure of the rest of the molecule. This view would suggest that the same smell might indeed result from different molecules having different microscopic components

Such questions could be answered more definitively by biochemists and neurophysiologists. But whatever the outcome of this case, the question of the supervenience of chemistry on physics would seem to depend precisely on the empirical facts, and the conclusions which they support, that are to be drawn from cases like the one considered above, and not from more general philosophical musing about chemistry and physics. Indeed, if the alleged supervenience of chemistry on physics is meant to provide an exemplar for the supervenience relationship (and as such a stringent test case for the more far-reaching question of the supervenience of biology on physics, or mental states on physical states) more work within what may now be thought of as the Philosophy of Chemistry seems in order.

Thus, we hope by now to have established the following two conclusions: (1) that there should be more scholarship within "The Philosophy of Chemistry" in its own right, given the unique light which it sheds on some of the most important debates within the philosophy of science, and (2) that there is much to be learned in the application of our conclusions from the case of chemistry to other debates within the "special sciences". In the next section, we shall briefly consider a few such issues, which the Philosophy of Chemistry raises for the Philosophy of Mind, and the Philosophy of Social Science.

7. LESSONS FOR THE SPECIAL SCIENCES

We shall now briefly consider the importance of the issues which the Philosophy of Chemistry has raised for such topics as reductionism, explanation, laws, and supervenience, in the application to existing debates within the Philosophy of Mind and the Philosophy of Social Science. What can the special sciences learn from the case of chemistry?

Perhaps the greatest source of interest which the philosopher of mind or the philosopher of social science may have in the philosophy of chemistry is simply to learn that, from a certain point of view, chemistry too can be considered a "special science". And attendant upon this is the realization that what previously may have been considered a relatively uncontroversial case of ontological dependence raises the very same issues regarding reducibility, the autonomy of explanations (nomological and otherwise) at secondary levels, and the appropriateness of supervenience, that have long dogged many of the traditional debates within the philosophy of mind and the philosophy of social science.

Far from suggesting, however, that chemistry provides a paradigm case of conceptual emergence, or unequivocal support for the autonomy of law-like relationships in a secondary science, our point here is merely that those who are interested in debates about the dependence of the mental upon the physical, the appropriateness or possibility of social scientific laws, and the implications of supervenience, have a lot to learn from chemistry. Here, after all, is a science whose ontological dependence upon physics is not in doubt. Chemistry suffers from none of the worries about "vital forces", "consciousness", or "intentionality" which have bedeviled the debate about laws in developmental and evolutionary biology or the social sciences. Yet, even given the purely material nature of the relationship between the subject matters of chemistry and physics, we note that many issues – like supervenience or the autonomy of law-like explanations – can here be studied in their purest form. Does strong ontological dependence not only allow epistemological autonomy, but also suggest that in some cases non-reductive explanations are preferable? If causal forces are discernible at the primary level, does this suggest that irreducible nomological explanations cannot also be rendered at the secondary level? How valuable is the concept of supervenience in allowing us to maintain material dependency while also supporting irreducibility?

Such questions can perhaps be analyzed in their purest form within the philosophy of chemistry, then to be applied back to debates within the special sciences. For instance the special scientist might ask: Does the sort of conceptual irreducibility we have supported within the philosophy of chemistry easily transfer to debates within the philosophy of mind?

Does the suggestion that one can favor autonomous nomological explanations within chemistry, while still recognizing the fundamental ontological dependence of chemical relationships upon physical ones, suggest that there can be laws in the social sciences?[27] Such questions represent an important source of interest which other philosophers may have in the philosophy of chemistry. No longer satisfied merely to draw examples from chemistry, to support whatever conclusion is desired in debates about the secondary sciences, we are here advocating that many of the concepts themselves have a richness which can be appreciated only by considering the facts of the unique relationship of chemistry to physics.

8. CONCLUSION

In this essay, we have offered several arguments in support of greater philosophical attention to what may now be called "The Philosophy of Chemistry". Such a field may pay rich dividends, not only for philosophical study about chemical topics in their own right, but also for the importance of the conclusions one might draw from this field for application to existing debates throughout the philosophy of science. We have here provided several suggestions for further work, and have appended a comprehensive bibliography of works that have to date appeared within the philosophy of chemistry, in order to allow such study now to go forward.

It has of late become a truism within the philosophy of science that *a priori* solutions to philosophical matters concerning the sciences are stale without attention to empirical details drawn from the sciences themselves. A corollary view might now also be offered: that what many have dismissed as straightforwardly empirical matters concerning the relationship between the sciences may also benefit from renewed philosophical attention.

NOTES

* The authors would like to thank James Woodward, Kim Sterelny and Jeff Ramsey for their comments on an earlier version of this article.

[1] Vol. 69, No. 3 (December 1986).

[2] Published in *PSA 1994, Vol. 1* (East Lansing, Mich.: Philosophy of Science Association, 1994).

[3] Even some of the studies purported to deal with the reduction of chemistry are in effect disguised studies into the foundations of quantum mechanics. In our view this is especially true in the work of Primas (1983).

[4] Despite the ubiquity of the term "reduction" in the philosophy of science, there is a fierce debate over how it should be defined. The classic definition can be found in Ernest Nagel, *The Structure of Science* (New York: Harcourt, Brace, and World, 1961). Perhaps

the most comprehensive analysis of the different possible senses of the term "reduction" can be found in Lawrence Sklar, 'Types of Inter-Theoretic Reduction', *British Journal for the Philosophy of Science*, Vol. 18 (1967), pp. 109–124. In the present paper we shall be interpreting reduction in the more traditional sense, as an epistemological relationship between scientific theories that bears directly on the issue of scientific explanation. It is our opinion, therefore, that talk of "ontological reduction" only confuses the issue. Cf. F. Ayala (1974) in *Studies in Philosophy of Biology*, F. Ayala and T. Dobzhansky (eds.), (Berkeley: University of California Press).

[5] We make no apologies for taking such an unavoidably piecemeal approach, which we understand will not be to the taste of some philosophers from the "old school" who believe that one should only deal in generalities and who might instinctively wish to avoid grappling with the sordid details of present day chemistry and physics.

[6] For an introduction to the literature on this debate, see the bibliography in Sklar, "Inter-Theoretic Reduction", cited in Note 4 above.

[7] New York: Harcourt, Brace, and World, 1961.

[8] The only experimental values admitted into genuine *ab initio* work are those of fundamental constants such as the mass and charge of the electron.

[9] A recent review of the work in ab initio quantum chemistry can be found in M. Head-Gordon, 'Quantum Chemistry and Molecular Processes', *Journal of Physical Chemistry* **100**, 13213–13225 (1996).

[10] Most practitioners of quantum chemistry do not consider this a serious criticism and continue to label the methods as ab initio although they are strictly speaking not so in the sense which we intend.

[11] Handy, N., (1992), 'Pople and Boys', *Chemistry in Britain* **28**, 709–709.

[12] Weinhold, F., (1972), 'Upper and Lower Bounds to Quantum Mechanical Properties', *Advances in Quantum Chemistry*, Vol. 6, 299–331.

[13] Even here one should perhaps remain agnostic regarding reduction, since it is not inconceivable that quantum mechanics will be replaced by a theory which admits exact solutions even in chemically interesting cases.

[14] One of us (Eric Scerri) has previously referred to this form of reduction as "pragmatic reduction". Scerri, E. R., 'Has Chemistry Been At Least Approximately Reduced to Quantum Mechanics?', *PSA 1994*, Vol. 1 (East Lansing, Mich.: Philosophy of Science Association), 160–170.

[15] Previous failure to draw such a distinction has resulted in much confusion regarding the status of claims about the reduction of chemistry.

[16] Some of these issues are discussed in the article by J. van Brakel in this issue.

[17] This claim is controversial and is disputed in the accompanying article by Ramsey, among others.

[18] Curiously, the opposite conclusion seems to have been reached in the field of chemical education. The fact that chemical explanations frequently appeal to electronic orbitals is wrongly taken as a reason for basing the presentation of chemistry on quantum mechanics. This is to commit the "orbital fallacy". E. R. Scerri (1991), 'Chemistry, Spectroscopy and the Question of Reduction', *Journal of Chemical Education*, Vol. 68, 122–126.

[19] Scerri, E. R., 'The Evolution of the Periodic Table', *Scientific American* (forthcoming).

[20] The length of the intervals between recurring elements varies throughout the periodic table being 2, 8, 8, 18, 18, 32, etc.

[21] The question of whether Mendeleev triumphed because of making predictions rather than for accommodating the properties of the elements known at the time has been the source of much discussion among philosophers of science interested in the debate regarding pre-

diction and accommodation of data by scientific theories. Several examples are: Brush, S. J. (1989) 'Prediction and Theory Evaluation', *Science* Vol. 246, 1124–1129; Gardner, M. R. (1982) 'Predicting Novel Facts", *British Journal for the Philosopy of Science*, Vol. 33, 1–15; Lipton, P. (1990) 'Prediction and Prejudice', *International Studies in the Philosophy of Science*, Vol. 4, 51–65; Maher, P. (1988) 'Prediction, Accommodation and the Logic of Discovery', *PSA 1988*, Vol. 1 (East Lansing, Mich.; Philosophy of Science Association), 273–285. The appropriate evaluation of the role of the periodic table regarding prediction and accommodation may be one example of the relevance of the philosophy of chemistry to work in the philosophy of science (Scerri, Worrall, in preparation).

[22] As Löwdin has written, "it is perhaps remarkable that, in axiomatic quantum theory, the simple energy rule (order of filling of orbitals) has not yet been derived from first principles". P. O. Löwdin (1969), 'Some Comments on the Periodic System of the Elements', *International Journal of Quantum Chemistry* **IIIS**, 331–334. Neither has this situation changed since Löwdin wrote these words.

Recently Rouvray has re-emphasized how quantum mechanics does not provide a true reduction of the periodic table. D. H. Rouvray (1996), 'The Surprising Periodic Table: Ten Remarkable Facts', *Chemical Intelligencer*, July: 39–47.

[23] In any case it is not clear precisely what Hettema and Kuipers intend by this phrase.

[24] See for example, Jaegwon Kim (1984), 'Concepts of Supervenience', *Philosophy and Phenomenological Research*, Vol. 45(2), 153–176. An excellent collection of current papers on supervenience can be found in Horgan, T. (1983) (ed.), 'The Spindel Conference: Supervenience', *The Southern Journal of Philosophy*, Vol. 22, Supplement.

[25] "Reduction, explanation, and the like are epistemic activities, and the mere fact that such equivalence or biconditionals 'exist' is no guarantee that they are, or will ever become, *available* for reductive or explanatory uses". J. Kim, 'Concepts of Supervenience', p. 173. It is interesting to note, however, that Kim no longer thinks that supervenience supports the non-reductionist program. Cf. his 'Mechanism, Purpose, and Explanatory Exclusion', in J. Tomberlin (1989) (ed.), *Philosophical Perspectives*, Vol. 3 (Atascadero, Calif.: Ridgeview), 77–108.

[26] *The Southern Journal of Philosophy* (1985), Vol. 23, 93–99. Teller answers this question in the negative.

[27] One of us (Lee McIntyre) has explored the question of the autonomy of social scientific laws in Chapter 6 of *Laws and Explanation in the Social Sciences* (Boulder, CO: Westview Press, 1996), where the analogy with chemistry is considered explicitly.

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Prediction of the Nature of Hafnium from Chemistry, Bohr's Theory and Quantum Theory

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Summary

The chemical nature of element 72, subsequently named hafnium, is generally regarded as a prediction from Bohr's theory of the periodic system and hence as a prediction from quantum theory. It is argued that both of these views and in particular the latter are mistaken. The claim in favour of Bohr's theory is weakened by his accommodation of independent chemical arguments and the claim in favour of quantum theory is untenable since the prediction is not strictly deductive.

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1. Introduction

In this article I consider a historical episode which is frequently taken as an example of a successful chemical prediction on the basis of quantum theory. Kragh has already given a detailed discussion of the discovery of hafnium from the point of view of the physics involved.[1] In the present article, I wish to widen the discussion to emphasize the chemical point of view and this will include a brief survey of chemistry textbooks of the period. The main motivation for the present study is to examine the role of physics when it is applied to chemical problems.[2] I will also endeavour to draw some philosophical conclusions from this historical episode regarding the epistemological reduction of chemistry to quantum theory, that is reduction in practice rather than just in principle.

I wish to argue that the usual claim as to the prediction of the true chemical nature of element number 72, subsequently named hafnium, does not represent as unam-

[1] H. Kragh, 'Chemical Aspects of Bohr's 1913 Theory', *Journal of Chemical Education*, 54 (1977), 208–10. H. Kragh, 'Niels Bohr's Second Atomic Theory', *Historical Studies in the Physical Sciences*, 10 (1979), 123–86.

[2] The present article forms part of a larger study which will also consider the role of the later quantum mechanics in chemistry.

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biguous a success for the theory as has been generally supposed.[3] In this paper I will take a conclusive or strict prediction to mean one which is made deductively from the postulates of a theory, or *ab initio* to use the contemporary terminology of quantum chemistry. A weak prediction will be taken to mean one which includes semi-empirical or even *ad hoc* elements.

The prediction and eventual confirmation that element number 72 is not a rare earth element is widely regarded as a triumph for Bohr's theory of the periodic system.[4] No doubt some grounds exist in support of this view, although I believe this to be a weak prediction as I shall argue. It is necessary to distinguish this prediction in the weak sense using Bohr's theory of the periodic system from any prediction in the strict sense from quantum theory. This would permit one to discuss another prevelant notion that, whereas chemists believed element 72 to be a rare earth, Bohr drew specifically on quantum theory to suggest otherwise. According to this view the discovery of hafnium is regarded as an early case of reduction of chemistry by quantum theory as distinct from the later quantum mechanics.

I will argue that both parts of this view are mistaken. Firstly, not all chemists believed that hafnium should be a rare earth and secondly Bohr's *prediction* was not very conclusive, was based on a highly empirical theory of electron shells, and was not a deductive argument from the principles of quantum theory.

My reasons for doubting that quantum theory, as distinct from other approaches, predicted that hafnium would be a transition metal rather than a rare earth, fall under the following broad categories;

(i) What I propose to call the counting argument.
(ii) The views of chemists at the time as to the supposed nature of element 72.
(iii) Bohr's writings on periodicity and more specifically on element number 72.

The first and second of these points will be discussed in section 2 and the third point in section 3.

[3] For example, Popper writes:

> I still remember vividly the excitement of the discovery of the element 72 (Hafnium) in 1922, as a result of Niels Bohr's marvellous quantum theory of the periodic system of elements. It struck us then as the great moment when chemistry had been reduced to atomic theory; and it was, I am still inclined to say, the greatest moment in all the reductionist adventures of the twentieth century, superseded perhaps only by the breakthrough represented by Crick and Watson's discovery of the structure of DNA.
>
> Bohr's theory led not only to the prediction to the chemical properties of elements, and thereby to the prediction of the properties of the still unknown element 72 and thus to its discovery, but it also allowed the prediction of some of their optical properties and it even led to the prediction of some of the properties of the chemical compounds

K. R. Popper, *The Open Universe*, edited by W. W. Bartley, 3 vols (London, 1982), III, 163-4.

[4] The quotation from Popper (footnote 3) provides a good example.

2. Chemical aspects

2.1. *The counting argument*

The prediction that hafnium is not a rare earth element can be obtained quite simply by counting and is by no means dependent on assuming electron shells. It had been known for some time that the number of elements in each period follows a definite sequence given by 2, 8, 8, 18, 18, 32 (probably followed by 32), etc.[5]

By adding the first six of these numbers one arrives at the conclusion that the sixth period terminates with a noble gas of atomic number 86. It is a simple matter to work backwards from this number to discover that element number 72 should be a transition metal and a homologue of zirconium, which shows a valency of four. This procedure depends on the plausible assumption that the third transition series should consist of ten elements as do the first and second transition series.

72,	73,	74,	75,	76,	77,	78,	79,	80,	81	.....	82,	83,	84,	85,	86
			..... 10 transition metals								IV	V	VI	VII	VIII
1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th		main group elements				

However any implementation of the counting argument hinges on a definite knowledge of the number of elements present. This information was not available before the work of Moseley in 1914, who obtained the correct order and left the appropriate gaps in the sequence of elements from lanthanum to tantalum.[6] Consequently the counting argument could only have been used with confidence in the period between 1914 and 1923, the latter being the date of the eventual discovery and characterization of hafnium. It should be noted, though, that Moseley's work was by no means immediately accepted.[7]

On the other hand the 'forward counting argument' proved to be more complicated. Even if chemists were prepared to accept the existence of the correct number of rare earths as reported by Moseley, the use of forward counting was problematical due to the ambiguous classification of cerium. This element, one of the oldest known rare earths, displays a quite unmistakable quadri-valency in its chemical properties. As a result cerium was often tabulated with elements in group IV and was not strictly regarded as a rare earth.

[5] J. R. Rydberg discovered the $2n^2$ rule in 1906 for the number of elements in successive periods. This was not published until 1914. J. R. Rydberg, French translation from Swedish original in *Journale de Chimie Physique*, 12 (1914), 585. Rydberg originally thought that the number of elements in each period was given by the sequence, 2, 2, 8, 8, 18, 18, 32,... However the number 2 is not repeated twice, unlike all the others. The error arose from regarding nebulium and coronium as the third and fourth elements. They were later shown to be highly ionized forms of oxygen and iron respectively.

[6] Letter from H. G. J. Moseley to G. von Hevesey, 23 April 1914, quoted in J. L. Heilbron, *H. G. J. Moseley: The Life and Letters of an English Physicist, 1887–1915* (Berkeley, Calif., 1974), p. 234. While some authors such as Bassett believed that there might be eighteen rare earths, Thomsen anticipated the correct value of 14 before the work of Moseley, as did Preyer. H. Bassett, 'A Tabular Expression of the Periodic Relations of the Elements', *Chemical News*, 65 (1892), 19. H. P. J. J. Thomsen, 'Classifications des corps simples', *Oversigt Kongelige Danske Videnskabernes Selskab*, 132–6. W. Preyer, *Das genetische System der Elemente* (Berlin, 1893).

[7] Vickery's chemistry textbook states many chemists were unwilling to accept Moseley's work or to apply it to the lanthanide elements; R. C. E. P. Vickery, *Chemistry of the Lanthanons* (London, 1953), p. 8.

For example, Mellor skips cerium and starts the rare earths at praseodymium. By counting fourteen rare earths in this way he arrives at the conclusion that the predicted element 72 would be the last of the rare earths.

> The fourteen elements (two of which remain to be discovered) which have interpolated themselves in the middle of this period (suggesting one of those unaccountable 'sports' of Nature) are metals of the rare earths; elements which are not only extremely rare, but which resemble one another so closely that their identification, and still more their separation, is extraordinarily difficult.[8]

He then gives the following list of these elements, with their atomic numbers and weights:

				59	**60**	**61**
				Pr	Nd	?
				140	144	—
62	**63**	**64**	**65**	**66**	**67**	**68**
Sa	Eu	Gd	Tb	Dy	Ho	Er
150	152	157	159	162·5	163·5	167·7
69	**70**	**71**	**72**			
Tm	Yb	Lu	?			
168·5	172	175	—			

In this as well as in another table,[9] Mellor is careful to group elements together by chemical properties and his missing element 72 is found in group IV of a short form periodic table which includes titanium and zirconium as well as cerium. The grouping of element 72 with zirconium and titanium is tantamount to regarding element 72 as a transition metal.

A textbook by Smith-Hopkins is also interesting with regards to this issue. The author states:

> The term 'rare earth group' is a rather indefinite one because there are no very sharply drawn boundary lines. Strictly speaking, the term should include the following elements; praseodymium, ekaneodymium (undiscovered), samarium, europium, gadolinium, terbium, holmium, dysprosium, erbium, thulium, ytterbium (neoytterbium), lutecium and celtium?[10]

As in the case of Mellor, this classification skips cerium before beginning what it regards to be the true rare earths and consequently predicts that element 72 should be a rare earth. Further pasages in the Smith-Hopkins text shows the extent of complications regarding which elements should be considered as rare earths,

> Almost invariably cerium is also included, mainly because in its trivalent compounds it is also a typical rare earth. Thorium is likewise generally treated with the rare earth group, because it is found associated with them in nature and

[8] J. W. Mellor, *Modern Inorganic Chemistry* (New York, 1918), pp. 116–18.
[9] Ibid., p. 117.
[10] J. Smith-Hopkins, *Chemistry of the Rarer Elements* (Boston, Massachusetts, 1923), pp. 93–4.

resembles cerium closely. It seems more logical, however, to regard thorium as an element which is closely related to the rare earth group, but not strictly speaking a member of it.[11]

Another interesting case can be found in the textbook by Partington,[12] which is in turn based upon the periodic table of Harkins and Hall.[13] In these versions we find lanthanum as the first rare earth, followed by cerium which is placed in group IV of a short form periodic table. The rare earths are taken as starting with lanthanum. The following element, cerium, is regarded as a rare earth although it appears in group IV of the table. The remaining twelve rare earths are all placed together with lanthanum. As a result of this procedure lutetium is found to be the final rare earth, thus implying correctly that hafnium would be a transition metal. Indeed, Partington predicts a new element between lutetium and tantalum with a mass of about 177 and he clearly states that it lies beyond the rare earths.[14] However, in doing so Partington as well as Harkins and Hall appear to make an error in that they fail to count an element which they themselves state would be expected to occur between neodymium and samarium. Had this element been included in the count of rare earths, they would have found the last of the rare earths to be ytterbium, which would even have placed element number 71 beyond the rare earths.[15]

To summarize the counting argument, this form of reasoning was available to chemists in the period from 1913–1914 to 1923 in two forms. On could either assume the lengths of periods as given by Rydberg and utilize a backward counting argument to arrive at the correct conclusion that element 72 would be transitional, that is beyond the rare earths. The second possibility was a forward counting argument based on the knowledge of there being fourteen rare earths. This argument depended on exactly which elements were actually classified as rare earths and consequently were not as clear-cut in predicting the chemical nature of element 72. As we have seen, such forward counting arguments as given by Mellor and Partington, for example, reached opposite conclusions as to the chemical nature of hafnium.

2.2. *Views of chemists, pre 1923, on the nature of element 72*

The notion that element number 72 was not a rare earth was already held by a number of chemists. Element 72, or at least the vacant space which it was supposed to fill, was often placed beyond the rare earth block published periodic tables prior to Bohr's theory. In 1895, a Danish chemist, Thomsen, produced a periodic table which correctly included fourteen rare earths and also associated the element before tantalum, with zirconium. [16] Thomsen, who is known to have had an influence on Bohr, thus became one of the first chemists to correctly predict that element 72 would be a transition metal rather than a rare earth.

[11] Ibid., p. 94.

[12] J. R. Partington, *A Textbook of Inorganic Chemistry* (London, 1921).

[13] W. D. Harkins and R. E. Hall, 'The Periodic System and the Properties of the Elements', *Journal of the American Chemical Society*, 38 (1916), 169–221.

[14] Partington (footnote 12), 461.

[15] Interestingly, this corresponds to modern thinking on classification of the elements contrary to the vast majority of published periodic tables in which lutetium is wrongly shown as the last of the rare earths. W. B. Jensen, 'The positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table', *Journal of Chemical Education*, 59 (1982), 634–6.

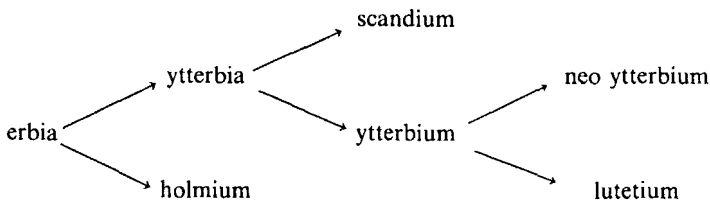
[16] Thomsen, (footnote 6).

The Welsh chemist Bury makes the following specific prediction as to element 72:

> Between lutecium and tantalum an element of atomic number 72 is to be expected. This would have the structure (2, 8, 18, 32, 8, 4), and would resemble zirconium.[17]

I would suggest that contrary to the accounts of Bohr's heroic prediction, few chemists believed that element 72 was in fact a rare earth. Those who did were the few who specialized in obtaining rare earths by the painstaking separation of certain mineral ores and it is only reasonable that according to developments in that field they should have thought that element 72 would be another such rare earth.

In 1879, Marignac showed that the rare earth erbia could be separated into two rare earths, ytterbia and another element later called holmium. A year later ytterbia was separated into two distinct elements called scandium and ytterbium. The next step was taken by Urbain and von Welsbach who independently found that ytterbium itself could be separated into neo ytterbium (70) and lutetium (71). It was only natural that these workers should suspect the possibility of discovering further new elements by repeated separations of the same minerals.



Both Urbain and von Welsbach believed that ytterbium contained small amounts of a third rare earth which would possibly turn out to be number 72. Urbain announced a positive spectroscopic identification in 1911,[18] but his claim could not be confirmed by Moseley using his X-ray method.[19] Urbain revived his claim eleven years later, announcing that he and Dauvillier had used a more accurate X-ray experiment and had detected two weak lines,[20] whose frequencies corresponded approximately to those expected for element 72 on the basis of Moseley's law.[21]

[17] C. R. Bury, 'Langmuir's Theory on the Arrangement of Electrons in Atoms and Molecules', *Journal of the American Chemical Society*, 43 (1921), 1602–9 (p. 1608).

[18] G. Urbain, 'Sur un nouvel element qui accompagne le lutecium et le scandium dans les terres rares', *Comptes Rendus de l'Académie des Sciences de Paris*, 152 (1911), 141–3.

[19] Heilbron (footnote 6), p. 101.

[20] There was nothing in the observations themselves to indicate that the supposed new element was a rare earth element. The latter claim rested on the fact that the supposed element 72 had been found among minerals which had already yielded a number of rare earths.

[21] Even the mere presence of the two faint lines was disputed, and Siegbahn, a leading spectroscopist who inspected Urbain's X-ray plate, reported that he could not see the claimed evidence.

3. Bohr's writings on periodicity and more specifically on element 72

According to Bohr's account, the old quantum theory can be used to explain the periodic table in terms of the electronic structure of atoms.[22] However, even just a casual examination of Bohr's account of chemical periodicity shows that the periodic table cannot be deduced from theory. The alleged explanation is more of an exercise in accounting for the known chemical facts in terms of an alternative representation based on the approximate model of electronic configurations.

Contrary to Bohr's own claims, the configurations were arrived at by intuition and reference to chemical and spectroscopic behaviour rather than quantum theoretical principles.[23] This can be seen from the irregular manner in which Bohr populated the electron shells while trying to maintain agreement with the known experimental facts. For example the sudden rearrangement in the configuration of nitrogen appears to be an attempt to account for the trivalency of the element. Similar adjustments were made in oxygen and fluorine to ensure the predominant divalency and univalency of these elements respectively.

1	H	1		
2	He	2		
3	Li	2	1	
4	Be	2	2	
5	B	2	3	
6	C	2	4	
7	N	4	3	
8	O	4	2	2
9	F	4	4	1
10	Ne	8	2	
11	Na	8	2	1
12	Mg	8	2	2
..	..	.	.	.
18	Ar	8	8	2

Table 1. Adapted from Bohr's original scheme for electronic configurations of atoms[24]

Between the years 1921 and 1923, Bohr returned to the problem of atomic structure and the periodic table. He announced a new improved version of the electronic periodic table, claiming it to be based on a principle of the old quantum theory, namely the adiabatic principle.[25] His method, called the Aufbauprinzip, consisted in building up successive atoms by the addition of an extra electron to the previous atom. Bohr

[22] N. Bohr, 'On the Constitution of Atoms and Molecules, Part II; Systems Containing Only a Single Nucleus', *Philosophical Magazine*, 26 (1913), 476–502.

[23] Nevertheless, I do not deny that Bohr did carry out a number of calculations on this question.

[24] Bohr (footnote 22), p. 497.

[25] N. Bohr, 'Uber die Anwending der Quantumtheorie auf den Atombau I' *Zeitzschrift fur Physik*, 13 (1923), pp. 117–59. English translation in Niels Bohr, *Collected Papers* [hereafter NBCP], edited by J. Rud-Nielsen (Amsterdam, 1977), volume 3.

developed his new account of the periodic table according to the two quantum numbers n, the main quantum number, and k, the azimuthal quantum number. These numbers emerged from the quantum conditions and served to identify the stationary states of the system. According to this scheme an atom of sulphur for example, with sixteen electrons, would have an electronic configuration of 2, 4, 4, 6.

n	k	Total number of electrons
1	1	2
2	1	4
2	2	4
3	1	6
3	2	6
3	3	6

Table 2. Assignment of electrons to shells. Adapted from Bohr's later scheme[26]

Letters to Bohr following the publication of his theory of the periodic system in *Nature*[27] contain the following passages:

From Rutherford,

> Everybody is eager to know whether you can fix the rings of electrons by the correspondence principle or whether you have recourse to the chemical facts to do so[28]

and from Ehrenfest:

> I have read your article in *Nature* with eager interest.... Of course I am now even more interested to know how you saw it all in terms of correspondence.[29]

As several of the Göttingen physicists who were exposed to these ideas by Bohr's own lectures later commented, the work rested on a mixture of *ad hoc* arguments and chemical facts without any strict derivations from the principles of quantum theory to which Bohr frequently alluded.[30] As Kragh writes, it was realized in 1922 that Bohr's theory was not deductive,[31] although admittedly Bohr drew on the observed X-ray spectra of elements which were interpreted with the aid of quantum theory.

[26] N. Bohr, *The Theory of Atomic Spectra and Atomic Constitution, Three Essays* (Cambridge, 1924), p. 113.

[27] N. Bohr, 'Atomic Structure', *Nature*, 107 (1921), 104–7.

[28] E. Rutherford to N. Bohr, 26 September 1921, in Niels Bohr Archives, Copenhagen.

[29] P. Ehrenfest to N. Bohr, 1921, 27 September in NBCP vol. 4.

[30] W. Heisenberg as quoted by H. Kragh, 'Niels Bohr's Second Atomic Theory', *Historical Studies in the Physical Sciences*, 10 (1979), 123–86 (p. 61). H. Kramers, as quoted by H. Kragh, 'The Theory of the Periodic System', in *Niels Bohr a Centenary Volume*, edited by A. P. French and P. J. Kennedy, (Cambridge, Mass., 1985), p. 60.

[31] Kragh (footnote 30), second reference, pp. 60–1.

The notion that the periodic table can be strictly deduced from quantum theory appears to be completely untenable. This position is virtually conceded by Bohr when he states:

> On the general view of the formation of atoms however, and by making use of the knowledge of the properties of the corresponding elements, it will be attempted to ... obtain indications of what configurations of the electrons may be expected to be to occur in atoms.[32]

MacKinnon has aptly described Bohr's style,

> Bohr's explanation of the periodic table is the crowning achievement of the old atomic theory. It is also one of the clearest manifestations of the type of multifaceted nonlinear reasoning in which Bohr excelled. He was not attempting to deduce the periodic table from his atomic theory. He was, rather, trying to develop a consistent atomic account that fitted the data coming from radically diverse sources: atomic theory, spectral lines, ionization energies, X-ray spectra, the correspondence principle, the periodic properties of the elements, chemical valencies and information on valent and covalent chemical binding. In blending these together Bohr functioned more like a symphony director than a deductive logician.[33]

According to Bohr's theory, the rare earths are characterized by the building-up of the N group or the fourth electron shell from the nucleus. In this view, the first rare earth is cerium with a fourth shell configuration of,

$$\text{cerium (58)} \qquad (4_1)^6\ (4_2)^6\ (4_3)^6\ (4_4)^1$$

and the last rare earth is lutetium with the following configuration,

$$\text{lutetium (71)} \qquad (4_1)^8\ (4_2)^8\ (4_3)^8\ (4_4)^8$$

The completion of the fourth shell represents the end of the rare earth series and the next element which was as yet undiscovered was expected to be a transition metal and a homologue of zirconium, showing a valency of four.[34]

As noted earlier, the general approach used by Bohr in his assignment of electron shells was to ensure an overall agreement with the known periodic table.[35] The form of the chemical periodic table in fact guided Bohr to the electronic configurations.

The above quoted remarks from Bohr's contemporaries seem to be particularly true with regards to element number 72 for which Bohr never produced any mathematical arguments or any other form of argument resting specifically on quantum theory. My own search for Bohr's *predictions* regarding the electronic arrangements of the rare earths and that of hafnium has revealed the following;

[32] Bohr (footnote 22), 486.

[33] E. M. MacKinnon, *Scientific Explanation and Atomic Physics* (Chicago, 1982), p. 178.

[34] The rare earths show a marked tendency towards tri-valency. See for example J. D. Lee, *Concise Inorganic Chemistry* (New York, 1977), p. 395.

[35] Bohr favoured the Thomsen periodic table (footnote 6) with which he had become familiar in his university chemistry lectures.

First of all there are vague arguments based on 'harmonic interaction', correspondence and symmetry such as:

> Even though it has not yet been possible to follow the development of the group [rare earths] step by step, we can even here give some theoretical evidence in favour of the occurrence of a symmetrical configuration of exactly this number of electrons. I shall simply mention that it is not possible without coincidence of the planes of the orbits to arrive at an interaction between four sub-groups of six electrons each in a configuration of simple trigonal symmetry, which is equally simple as that shown by these sub-groups. These difficulties make it probable that a harmonic interaction can be attained precisely by four groups containing eight electrons, the orbital configurations of which exhibit axial symmetry.[36]

In a somewhat less obscure fashion Bohr uses the counting argument mentioned earlier in order to arrive at the conclusion that element 72 should not be a rare earth:

> As in the case of the transformation and completion of the 3-quanta orbits in the fourth period and the partial completion of the 4-quanta orbits in the fifth period, we may immediately deduce from the length of the sixth period the number of electrons, namely 32, which are finally contained in the 4-quanta group of orbits. Analogous to what applied to the group of 3-quanta orbits it is probable that, when the group is completed, it will contain eight electrons in each of the four subgroups.[37]

According to Bohr the element which represents the completion of the 4-quanta groups and therefore marks the end of the rare earths is lutetium with the following grouping of 4-quanta electrons:

$$\text{lutetium (71)} \quad (4_1)^8\ (4_2)^8\ (4_3)^8\ (4_4)^8$$

This element therefore ought to be the last in the sequence of consecutive elements with similar properties in the first half of the sixth period, and at the place 72 an element must be expected which, in its chemical and physical properties, is homologous with zirconium and thorium.[38]

He then adds:

> This which is already indicated on Julius Thomsen's old table, has also been pointed out by Bury.[39]

In his Göttingen lectures on the periodic table Bohr alluded to a calculation concerning the rare earth configurations:

> We can ascertain by a calculation that, with increasing nuclear charge, there will not only come a moment when an electron is bound more firmly in a 5_3-orbit than in a 6_1-orbit but that from a certain nuclear charge onwards, a 4_4-orbit will correspond to a firmer binding than a 5_1-orbit.[40]

[36] Bohr (footnote 26), 110.
[37] Ibid., p. 110.
[38] Ibid., p. 114.
[39] Ibid., p. 114.
[40] N. Bohr, 'Sixth lecture of seven lectures on the theory of atomic structure', Göttingen (1922), in NBCP, vol. 4, (p. 404).

This form of calculation was never produced by Bohr, nor has anything of the sort ever been found in the Bohr archives.

Bohr also expressed a certain amount of doubt over his prediction that hafnium would not be a rare earth. Having explained the filling of the 4-quanta groups as described above he says:

> However the reasons for indicating this arrangement are still weaker than in the case of the 3-quantic group and the preliminary closure of the 4-quantic group in silver.[41]

When Urbain and Dauvillier claimed to have discovered element 72 and that it was a rare earth, Bohr's initial response was to doubt his own prediction that it lay beyond the rare earths. This wavering was expressed in letters to colleagues as well as in the appendix of a book on atomic constitution. He wrote to Franck:

> The only thing I know for sure about my lectures in Göttingen is that several of the results communicated are already wrong. A first point is the constitution of the element 72, which, as shown by Urbain and Dauvillier, contrary to expectations has turned out to be a rare earth element after all.[42]

and to Coster:

> The question is apparently rather clear but one must of course always be prepared for complications. These may arise from the circumstance that we have to do with a simultaneous development of two inner electron rings.[43]

In the German edition of a book, *Drei Aufsatze uber Spectren und Atombau*, the appendix contained the following:

> Since the printing of these Essays I became acquainted with an investigation by Dauvillier concerning the X-ray spectra of some rare earths. From this it appears that the element with atomic number 72 is to be identified with the material Celtium whose existence had already been conjectured earlier by Urbain. The occurrence of this element in a fraction which contains the materials Ytterbium and Lutetium, would demand that the classification given in Fig. 5 is to be changed...
>
> Incidentally one must realise that the formation of the 4-quanta electron groups is only described in outline in the essay. In the question of the formation of this group in an atom of a given element within the sixth period we are concerned not simply with a comparison between the strengths of the binding of two single electrons in different types of orbits....[44]

[41] Ibid., p. 404.

[42] N. Bohr, Letter to J. Franck, 15 July 1922, Niels Bohr Scientific Correspondence, Niels Bohr Institute, Copenhagen, as quoted by H. Kragh, 'Niels Bohr's Second Atomic Theory', *Historical Studies in the Physical Sciences*, 10 (1979), 123–86.

[43] N. Bohr, Letter to D. Coster, 3 July 1922, Niels Bohr Scientific Correspondence, Niels Bohr Institute, Copenhagen.

[44] N. Bohr, *Drei Aufsatze uber Spectren und Atombau*, (Brunswick, 1922), p. 147. The translation from the German text was kindly provided by Professor H. R. Post.

Bohr soon returned to his original claim about element number 72. In doing so he provided further examples of his essentially chemical arguments for his views on the missing element. In referring to the claim by Urbain and Dauvillier, Bohr pointed out that if number 72 were a rare earth it should have a valency of three in common with other members of this group. Moreover, the following element tantalum, number 73 is known to have a valency of five.

> This would mean an exception to the otherwise general rule, that the valency never increases by more than one unit when passing from one element to the next in the periodic table.[45]

In response to the French claims, which they believed to be unfounded, von Hevesey and Coster working at Bohr's institute in Copenhagen began a search for element 72 in the ores of zirconium. Even their first attempt proved to be unexpectedly successful. After some further concentration of the new element, they obtained six clear X-ray lines whose frequencies were in very good agreement with Moseley's law applied to element number 72.[46] The new element was named hafnium after Hafnia, the Latin name for Copenhagen which had been the place of its discovery.

4. Conclusion

One of the misconceptions which seems to have arisen in connection with the hafnium episode is that Bohr himself set von Hevesey and Coster the task of searching for element 72 in the zirconium ores.[47] In fact, the search for hafnium, although carried out in the Bohr Institute, was undertaken independently by von Hevesey and Coster who wanted to surprise Bohr with the discovery of the new element. Furthermore, the first suggestion of where to look for element 72 came from the chemist Fritz Paneth, on the basis of chemical arguments.[48] Von Hevesey readily acknowledged his debt to Paneth in connection with the search for element 72, claiming that he would not have persevered had it not been for Paneth's encouragement.[49]

Of course when considering Bohr's prediction and from a logical point of view it does not matter who actually discovered the element or indeed who suggested where to search for the element. However I would still argue that these circumstances may be

[45] Bohr (footnote 26), p. 114.

[46] D. Coster and G. von Hevesey, 'On the missing element of atomic number 72', *Nature*, 111 (1923), 79.

[47] This claim has been made by a number of authors including Allsop and Klein. Klein's remarks are perhaps typical of the errors which creep into 'recollections' where genuine memories become confused with incorrect statements which the author might have read. R. T. Allsop, 'Element 72–the great controversy', *Education in Chemistry*, 10 (1973), 222–3. O. Klein, in *Niels Bohr: His Life and Work as seen by his Friends and Colleagues*, edited by S. Rozental (Amsterdam, 1967).

[48] F. A. Paneth, 'Das periodische System, Ergebnisse der Exakten', *Naturwissenschaften*, 1 (1922), 362–403 (p. 383). As Kragh (footnote 1, second reference) and van der Vet have stated, Paneth was one of the early supporters of Bohr's theory. P. E. van der Vet, 'The Aborted Takeover of Chemistry by Physics', (PhD thesis, University of Amsterdam, 1987). This seems to be as much connected with their personal acquaintance than with any deep appreciation which the chemist Paneth might have had for the technical details of Bohr's theory. I learned this from Paneth's son Heinz, who is now called Heinz Post. It should also be remembered that the priority dispute over element 72 took on something of a nationalistic flavour. On the Teutonic side were Bohr, Paneth, von Hevesey (although he was of Hungarian origin) and Coster, while the Gallic side was represented by Urbain, Dauvillier, and Maurice de Broglie among others.

[49] G. von Hevesey, unpublished memoir dated July 1923, kept at Niels Bohr Institute, Copenhagen (1923).

significant in setting Bohr's convictions about the nature of hafnium into context. Had Bohr really requested the search for the new element, perhaps this could be taken to support his confidence in the alleged prediction as to the nature of element 72. This was not the case, however, and as argued above, he expressed a certain amount of doubt over the prediction itself. The discovery of hafnium represented something of an unexpected bonus for Bohr's theory. As Kragh mentions in passing: 'The discovery of hafnium was only remotely related to Bohr's theory.'[50]

The news of the discovery itself was relayed by von Hevesey in a telephone conversation to Bohr in Stockholm where Bohr was about to receive his Nobel prize. As a result, the ceremony was delayed for half an hour and Bohr duly mentioned the discovery of the new element in the closing moments of his acceptance speech.

No doubt, Bohr's theory stimulated the eventual true discovery of element 72, but in view of all the factors described above it can still be doubted whether this development represents a successful, *ab initio* chemical prediction on the basis of quantum theory. Had Bohr's theory really made a prediction which had gone against the chemists of the day, and which had turned out to be correct, then the claim would be stronger. This was not the case however. It might be more accurate to say that the view held by some chemists that hafnium would not be a rare earth was rationalized or accommodated by Bohr's quantum theory of periodicity which possessed a somewhat *ad hoc* nature. Alternatively, if the term prediction is to be construed in a weaker sense than meaning an *ab initio* prediction, it might be true to say that Bohr's theory including all its inductive elements did predict the nature of hafnium whereas quantum theory itself did not.

I believe that the findings of this paper are relevant to the question of the epistemological reduction of chemistry, that is reduction in practice rather than in principle. A considerable amount of work has been carried out on the question of reduction of chemistry, both in principle and in practice, to quantum mechanics.[51] Very little has been done however with regards to chemistry and the earlier quantum theory. I suggest that the hafnium episode represents one of the few specific instances of an attempted reduction of a chemical fact to quantum theory. As I have argued in this article, I believe that this is a failed reduction in that it does not constitute an *ab initio* approach. Of course this episode has no bearing on the question of whether chemistry can be reduced in principle (ontological reduction) to quantum theory or quantum mechanics.

[50] H. Kragh, 'Niels Bohr's Second Atomic Theory', *Historical Studies in the Physical Sciences*, 10 (1979), 123–86.

[51] P. A. Bogaard, (The Limitations of Physics as a Chemical Reducing Agent', *Proceedings of the Philosophy of Science Association*, 2 (1978), 345–56. M. Bunge, 'Is Chemistry a Branch of Physics?', *Zeitschrift allgemeine Wissenschaftestheorie*, 13 (1982), 210–23. G. Del Re and C. M. Leiegener, 'The Relation of Chemistry to Other Fields of Science: Atomism, Reductionism, and Inversion of Reduction', *Epistemologia*, 10 (1987), 269–82. H. Primas, *Chemistry, Quantum Mechanics and Reductionism*, 2nd edition, (Berlin, 1983). E. R. Scerri, 'Electronic Configurations, Quantum Mechanics and Reduction', *British Journal of Philosophy of Science*, 42 (1991), 309–25. E. R. Scerri, 'Correspondence and Reduction in Chemistry', *Correspondence, Invariance and Heuristics* (Boston Studies in Philosophy of Science, volume 148), edited by S. French and H Kamminga (Dordrecht, 1993), pp. 45–64.

The present findings may also be relevant to the long standing debate as to whether a prediction in the temporal sense should serve as a means of validating a theory.[52] As many authors have emphasized, predictions and retrodictions are logically equivalent. The only advantage offered by predictions is a psychological one.

Some philosophers like Popper[53] are much impressed by the predictive aspect of Bohr's theory in as much as it forecasted the nature of hafnium. I believe that Popper is misled by this aspect. If prediction in the temporal sense is considered to be crucial then the essentially chemical predictions, such as the use of counting arguments, would have to be judged as being equally valid forms of prediction, which clearly they are not. Judging the quality of predictions should not hinge on the element of forecasting but on how strictly the prediction from a theory has been made. I believe that the present case study gives another example of why prediction in the temporal sense should not be favoured over retrodictions, which are also sometimes termed predictions.

Acknowledgement

I would like to thank Professors Helge Kragh and Heinz Post as well as two anonymous referees for commenting on earlier drafts of this article.

I have recently become aware of two interesting papers by Professor Mansel Davies which lend further support to my case against Bohr and in favour of chemists with regard to the prediction of hafnium.[54]

[52] S. J. Brush, 'Prediction and Theory Evaluation', *Science*, 246 (1989), 1124–9. M. R. Gardner, 'Predicting Novel Facts', *British Journal for the Philosophy of Science*, 33 (1982), 1–15. P. Lipton, 'Prediction and Prejudice', *International Studies in Philosophy of Science*, 4 (1990), 51–65. P. Maher, 'Prediction, Accommodation and the Logic of Discovery', *Philosophy of Science Association*, 1 (1988), 273–85.

[53] Popper (footnote 3).

[54] M. Mansel Davies, 'Charles Rugeley Bury and his Contributions to Physical Chemistry', *Archive for History of the Exact Sciences*, 36 (1986), 75–90; M. Mansel Davies, C. R. Bury, L. Vegard and the Electronic Interpretation of the Periodic Table, A note', *Archive for History of the Exact Sciences*, 41 (1990), 185–7.

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Has Chemistry Been at Least Approximately Reduced to Quantum Mechanics?

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1. Introduction

In order to discuss the question of the reduction of chemistry it will be necessary to begin with a brief review of what philosophers mean by reduction in science. I follow most authors on this subject by starting with the writings of Nagel (Nagel 1961). As is well known, Nagel stipulates that two formal conditions, namely connectability and derivability should be fulfilled in order to say that reduction of theory T_2 to theory T_1 has occurred. In addition he stipulates a non formal condition, that the primary or reducing science should be supported by experimental evidence.

Furthermore Nagel considers that reductions occur in two main varieties which he calls homogeneous and heterogeneous respectively. In homogeneous reduction the terms used by the reducing theory are also common to the theory to be reduced. For example Galileo's science of freely falling bodies was conceived of as separate from the mechanics of celestial bodies. Nagel claims that Newton's theory of mechanics absorbed or reduced both of these theories. The reduction in question is considered to be homogeneous since no new concepts are needed to describe motion in the Newtonian theory than were used in the older forms of mechanics. In heterogeneous reduction the distinctive traits of some subject matter are assimilated into those of a set of quite different traits. Nagel sees this type of reduction as problematical and worthy of further analysis unlike homogeneous reduction.

We may note in passing that the question of the reduction of chemistry would presumably fall into the heterogeneous category according to Nagel's scheme since, as many authors have pointed out, some typically chemical terms cannot be found in quantum mechanical language. For example Primas has written,

> Many calculations have been extremely sophisticated, designed by some of the foremost researchers in this field to extract a maximum of insight from quantum theory. For simple molecules, outstanding agreement between calculated and measured data has been obtained. Yet, the concept of a chemical bond could not be found anywhere in these calculations. We can calculate bonding energies without ever knowing what a bond is! (Primas, 1983, 5)

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A number of criticisms of Nagel have appeared, which aim to sharpen the criteria for reduction. Some of these have been described as falling under the label of indirect reduction. For example Kemeny & Oppenheim claim that T_2 is not obtained in terms of T_1 as in Nagel's form of reduction. Instead one obtains identical observable evidence from T_2 and T_1 although T_1 can may predict more. (Kemeny & Oppenheim 1956)

Other authors deny that reduction of theories takes place at all. Popper would presumably argue that if a theory is refuted it can hardly be said to correspond to, or be derived from the reducing theory. In Popper's own words,

> Newton's theory unifies Galileo's and Kepler's. But far from being a mere conjunction of these two theories...it corrects them while explaining them. The original explanatory task was the deduction of the earlier results. It is solved not by deducing them but by deducing something better in their place. (Popper 1957, 33)

Then there are the radical critics of reduction. The early Kuhn holds that two competing theories cannot be compared because the terms used in each theory are incommensurable (Kuhn 1962). Also, for Kuhn all significant reductions are replacement reductions, where the reduced theory is replaced by the theory to which it reduces and not retained as a correct theory.

Meanwhile, in characteristic fashion, Feyerabend attacks both of Nagel's formal conditions for reduction (Feyerabend 1962). For example, Nagel considers that Galileo's laws of mechanics are reduced to Newton's laws in the sense that both conditions (connectability and derivability) are fulfilled.

With regards to connectability, Feyerabend claims that this feature often does not exist between successive theories. For example, in classical mechanics length is a relation that is independent of signal velocity, gravitational fields and motion of the observer. This meaning of length differs from the meaning of length in relativity theory in which it is dependent on all three of the above factors. Classical and relativistic length he says are incommensurable concepts. On the question of derivability, Feyerabend points out that in Galileo's laws of mechanics the acceleration of a freely falling body is constant whereas in Newton's mechanics, acceleration increases with decreasing distance from the earth. The two systems of mechanics are thus incompatible according to Feyerabend. His conclusion is that either (i) approximate reduction is possible but we must forego derivability as a condition for reduction, or (ii) reduction fails. Feyerabend eventually decides on the second option whereby reduction fails altogether.

The early Putnam has criticized Feyerabend on the question of derivability claiming that Nagel's requirement can be maintained provided that we accept approximations.

> It is perfectly clear what it means to say that a theory is approximately true, as it is clear what it means to say that an equation is approximately correct: it means that the relationships postulated by the theory hold not exactly, but with a certain specifiable degree of error. (Putnam 1965, 206-207)

I believe that Putnam's statement can be used to give a working definition of what constitutes approximate reduction and I will return to this statement in a later part of this article.

For the intervening sections however I wish to adopt an approach which I will call pragmatic reduction. I will attempt to examine the extent to which chemistry has

been reduced in the terms used by physicists and chemists themselves. The most overt attempts at reduction in chemistry have been made through the use of Schrödinger's time independent equation. In the purest or ab initio approach the aim is to calculate the properties of atoms and molecules entirely from first principles, without recourse to any experimental input whatsoever.[1] Another part of current theoretical chemistry is concerned with semi-empirical approaches in which some experimental data is introduced into calculations. However the present survey will not consider such semi-empirical work.

The following two quotations may serve to give the essence of the *ab initio* approach. Firstly there is a little known remark made by Langmuir in the course of a popular lecture in 1921, before the advent of quantum mechanics.

> These things mark the beginning, I believe, of a new chemistry, a deductive chemistry, one in which we can reason out chemical relationships without falling back on chemical intuition....I think that within a few years we will be able to deduce 90 percent of everything that is in every textbook on chemistry, deduce it as you need it, from simple ordinary principles, knowing definite facts in regard to the structure of the atoms. (Langmuir 1921)

Secondly, the much quoted passage from one of the founders of quantum mechanics, Dirac, who put the case for ab initio calculations somewhat optimistically,

> The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble. (Dirac 1929)

2. Quantum Chemistry

The time-independent Schrödinger equation may be expressed in its most compact form as,

$$H\psi = E\psi$$

where H is the Hamiltonian operator concerning the kinetic and potential energy of the system, ψ is the wavefunction, which is a function of the coordinates of all the particles in the system and E is the observable energy of the system.

For a hydrogenic atom, that is a one-electron system such as the hydrogen atom, the He^{+1} ion or the Li^{+2} ion, the equation takes the form,

$$(-\hbar^2/2\mu\nabla^2 - Z e^2/r)\psi = E\psi$$

where $\hbar$ is Planck's constant divided by 2π and μ is the reduced mass of system. In the case of the hydrogen atom $\mu = m_n \cdot m_e / m_n + m_e$, ∇^2 or $(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)$ is the operator for the kinetic energy, Z is the nuclear charge, e the electronic charge and r the distance between the nucleus and the electron.

The solution to this one-electron equation is exact and characterized by three integers n, ℓ and m, the quantum numbers (Pauling, Wilson 1935).

$$\psi_{n,\ell,m}(r,\theta,\varphi) = R_{n,\ell}(r) \cdot \Theta_{\ell,m}(\theta) \cdot \Phi_m(\varphi)$$

The ground state wavefunction, that is the solution corresponding to $n = 1$, $\ell = 0$ and $m = 0$, is found to be,

$$\psi_1 = 1/\pi^{1/2}(Z/a_0)^{3/2}\, e^{-\rho/2}, \text{ where } \rho = (2Z/na_0)r, \text{ and } a_0 = h^2/4\pi^2\mu e^2.$$

Another solution includes the case where $n = 2$, $\ell = 1$, $m = -1$,

$$\psi_{2p(-1)} = 1/4(2\pi)^{1/2}\,(Z/a_0)^{5/2}\, re^{-Zr/2a_0} \sin\theta\; e^{-i\varphi}$$

These so called 'orbitals' are related to electron clouds encountered in elementary chemistry courses. The energies permitted for a hydrogenic atom are found to be,

$$E = -\mu Z^2e^4 / 2\hbar^2n^2 = -Z^2/n^2.\, W_H$$

where W_H is the energy for the ground state of the hydrogen atom or 13.60 eV.

The time-independent Schrödinger equation for atomic, ionic or molecular systems containing two or more electrons does not yield exact solutions and approximation methods must be employed. To consider the simplest such atomic case, the helium atom, the time-independent Schrödinger equation for the system is,

$$(-\hbar^2/2m_e\,\nabla_1^2 - \hbar^2/2m_e\,\nabla_2^2 - Ze^2/r_1 - Ze^2/r_2 + e^2/r_{12})\,\psi = E\,\psi$$

This differential equation cannot be solved by the method of separation of variables because of the presence of the term e^2/r_{12} which represents the inter-electronic distance. A good approximation method consists in the variation approach in which a trial function φ is chosen which contains variable parameters. It can be shown that the energy corresponding to this trial function E, is larger or equal to the exact ground state energy for the system E_0 (Pauling, Wilson, 1935).

$$E = \int \varphi^* H \varphi\, d\tau \geq E_0$$

where H represents the true Hamiltonian for the system.

For example, an approximate wavefunction for the helium atom can be taken to be,

$$\varphi = \varphi_1\varphi_2 = (Z'^3/\pi)\, e^{-Z'r_1}\, e^{-Z'r_2}$$

that is the product of two one-electron functions, each containing a variable parameter Z'. Evaluation of these integrals and minimization with respect to Z' gives the energy for the ground state of the helium atom as - 77.45 e.V. This result represents an error of approximately 2%.

Perhaps the most commonly used approximation in quantum chemistry is the Hartree-Fock method in which the wavefunction consists of an anti-symmetric product of one-electron functions, to take account of the permutation of electrons as dictated by the Pauli exclusion principle. It is assumed that each electron moves in the average field due to the nucleus and all the other electrons in the system. For the helium atom the required wavefunction takes the form of the determinant of a 2 x 2 matrix,

$$\psi = 1s(1)\alpha(1)1s(2)\beta(2) - 1s(2)\alpha(2)1s(1)\beta(1)$$

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The so called Hartree-Fock equations represent a pseudo-eigenvalue problem which requires an iterative approach and for which the use of computers is ideally suited. The total energy of the helium atom calculated in this way shows an error of approximately 1.5% as compared with the experimental value.

The atomic energies calculated by the Hartree-Fock method typically show errors of approximately 1% when compared with experimental atomic energies. Such relative errors of 1% may not appear to be very significant, but since the energy of a typical atom in its ground state is about 1000 e.V., the absolute error represents about 10 e.V. This is of the same order of magnitude as a typical chemical bond. The Hartree-Fock method can therefore fail to predict chemical bonding and it becomes necessary to resort to more accurate methods of approximation in order to obtain chemically meaningful predictions. Nevertheless, the Hartree-Fock wavefunction serves as a point of departure in more elaborate approximation methods.

In the so called Configuration Interaction method more than a single determinant is used to represent the wavefunction of the system. The wavefunction for the helium atom, for example, is now represented by a linear combination of determinants,

$$\psi = c_1 D_1 + c_2 D_2 + ...$$

and the computational procedure consists in minimising the energy by variation of the mixing coefficients or c_i's. The additional determinants are formally excited states of the helium atom. Whereas in the helium atom the ground state configuration is $1s^2$, two excited configurations might be $1s^1 2s^1$ and $1s^1 2p^1$.

Other methods which go beyond the Hartree-Fock level of approximation include Cluster Methods and Many-Body Perturbation Theory (Wilson 1984). These approaches involve the introduction of repulsion effects due to simultaneous interactions between three, four, and even more electrons in the expansion of the wavefunction. One important drawback of cluster methods and many-body perturbation theory is that they are not variational. That is to say, the calculated energies no longer represent upper bounds and it is possible to obtain predictions in excess of 100% of the experimental values. Nevertheless, their use is capable of reducing the error in the calculation of the energy of the helium atom to something of the order of 10^{-3} %.

We might just pause at this point in order to take stock of the progress made in the light of the original question as to how successfully chemistry has been reduced to quantum mechanics. It has to be said that the calculation of the ground-state energy of an atom carried out completely from first principles and to an accuracy of 10^{-3} % does seem to provide an argument in favour of the reduction of atomic chemistry, at least with regards to the reduction of a physically measurable quantity. However, I believe that it is necessary to adopt a more critical attitude to such claims especially in view of the computational approaches which are used and which are examined further in the following section.

3. Convergence and Error Bounds

Provided that increasingly larger linear combinations of atomic orbitals are taken, the experimental energy of the atom may be approached ever more closely. This is not surprising due to completeness property of series expansions (Pauling, Wilson 1935). Authors in modern theoretical chemistry often make a virtue of being able to guess the correct procedure by a mixture of intuition and past experience. The usual means of proceeding with a calculation appear to be somewhat ad hoc in this sense.

The common approach used in all these approximations is one of expansion of the wavefunction for the system as an infinite series of one-electron functions. In using such a procedure it is essential that the series used in the expansion should converge to the function which it is meant to represent. It is often assumed that with a sufficiently flexible trial function the results will eventually converge to the exact solution. Otherwise convergence is checked, up to a point, by examining the results of successive approximations.

However, there is no guarantee that, although the experimental value is being approached, the next level of accuracy might not show a sudden divergence. Such occurrences are not unknown in mathematical physics. Ideally, a general proof of convergence is required, which is independent of the data arising from any particular approximation in any particular case. The present lack of such convergence proofs in quantum chemistry must be recognized to mar any claim in favour of strict reduction.

From a pragmatic point of view however, it must be admitted that the convergence problem is no longer so pressing, since most modern computer packages such as the Gaussian series contain built-in convergence checking procedures.

The second problem which I wish to pint out is more serious. Although a variational calculation gives an upper bound to the exact solution it does not tell us how close we are to the true value. As is well known, error limits are demanded of experimental results as a matter of course. As Weinhold writes, perhaps one should also ask for a corresponding standard of reliability from the theoretical side (Weinhold,1972).

A general method of improving the situation would consist in finding a way to calculate both upper and lower bounds to the energy of any particular system under consideration. If this form of 'bracketing' were possible, it would endow quantum mechanics with a genuine power of prediction. The problem has been that whereas variation methods provide an upper bound to the energy as can readily be proved, sufficiently general and tractable method for determining lower bounds in cases applicable to atomic systems are not available. To sum up, what is needed in theoretical chemistry, is an independent non-empirical method of assessing the accuracy of the calculations[2].

4. The case of the CH_2 molecule

Although the early predictions made in quantum chemistry were generally unreliable, it has been forcefully argued that since 1970 quantum chemistry has "come of age" (Goddard, 1985). This arose from theoretical predictions on the geometry of the methylene molecule CH_2. This short lived and highly reactive molecule is unusual in having two unpaired electrons around the carbon atom as compared with the better known methane molecule in which all four of the outer electrons are said to be shared with electrons from four hydrogen atoms.

Various calculations carried out for methylene suggested that the molecule should be bent[3]. The molecule was first observed spectroscopically by Hertzberg who contrary to the theoretical predictions found it to have a linear shape. A more accurate treatment the following year by Bender and Schaefer put the angle in methylene at 135.1° (Bender, Schaefer, 1970). Three new experiments by independent groups finally confirmed (pace Popper) a bent geometry in methylene.

In 1971 Hertzberg re-examined his data and was forced to concede that he had previously been wrong and that his own experiment was also in keeping with a bent geometry. This change of mind on the part of Hertzberg has been frequently been ex-

ploited by Schaefer, who concludes that his own work represented a successful challenge against the findings of the world's leading spectroscopist.

I now turn to the claimed landmark paper of Bender and Schaefer. Firstly, to take up a general objection which was raised earlier, Bender and Schaefer do not produce any proof of convergence but merely examine convergence up to a certain point. In fact the authors applied computational methods developed earlier by Bender and Davidson but a key passage in this earlier paper betrays a rather serious drawback;

> The main difficulty in the selection of configurations...was of course the enormous number of possible configurations. In a typical calculation there are billions of configurations which can be formed with the correct symmetry. For an unfortunate choice...all of these might be equally important, but for a good initial guess only a few will really contribute to the wavefunction. (Bender, Davidson 1966, 2676).

Any procedure which relies on initial guesses must surely be judged to be essentially ad hoc and this raises doubts as to the extent to which chemical phenomena are being reduced in such supposedly ab initio calculations. Schaefer and co-workers also claim in a later paper that they set out to attempt to place error bars on the theoretical prediction of the bond angle. (McLaughlin, Bender, Schaefer, 1972). By employing an even larger basis set than the previous calculation, the authors estimate a bond angle of 134±2°. However, a detailed examination of the original source reveals a somewhat different picture for this claimed determination of error bars. To quote the authors:

> To aid our evaluation of the expected reliability of this 134° CH_2 angle, we point to the comparable first order calculations on the ground and excited states of NH_2, which yielded bond angles differing by 0.6 and 0.7 degrees from experiment values. In the light of these results and the H_2O results discussed above we estimate our theoretical bond angle of 134° is accurate to within 2°. (McLaughlin et al. 1972, 356-7)

Clearly, this approach represents an extrapolation from the application of the method from one molecule to that of another, and not a rigorous determination of error bars for the CH_2 molecule itself. In fact these calculations on CH_2 represent a perfect example of what Davidson has described as calibrated ab initio, as opposed to true ab initio work (Davidson 1984, 8-9)

5. The Si_2C story

In 1964 the molecule of Si_2C was first observed by infra-red spectroscopy (Veltner, McLeod, 1964). About twenty years later the fundamental Si-C symmetric stretching frequency was identified at 658 cm^{-1} (Kafafi et al. 1983). Shortly afterwards the molecule was studied theoretically and a value of 823 cm^{-1} was obtained for the symmetric stretching frequency (25% error). The authors did not however presume to challenge the assignment of the 658 cm^{-1} line (Grev, Schaefer 1985).

More recently another experimental group has identified the symmetric Si-C stretching mode with a new line at 840 cm^{-1} contrary to the earlier experiments (Presilla-Marquez, Graham 1991). In 1992 Schaefer and colleagues returned to the calculation to determine which line, the one at 658 cm^{-1} or at 840 cm^{-1}, is the true symmetric stretching mode. This provides an example of a state-of-the-art quantum chemistry calculation by one of the leading practitioners. The results obtained using various levels of approximation are tabulated below;

	$[\omega_1 - \nu_1/\nu_1] \times 100$.	$[\omega_3 - \nu_3/\nu_3] \times 100$	Energy (eV)
TZ+ 2P SCF	1.4 %	17.9 %	- 615.64079
TZ + 2P CISD	2.4 %	9.2 %	
TZ + 2P CCSD	0.9 %	5.2 %	
TZ + 2P CCSD (T)	-2.6 %	1.2 %	
TZ + 2P + f SCF	-4.3 %	21.3 %	- 615.64462
TZ + 2P + f CISD	5.2 %	9.4 %	
EXT + 2P SCF	1.0 %	17.9 %	- 615.65611
EXT + 2P + f SCF	-2.9 %	20.4 %	- 615.65925

Table 1. Percentage errors in the calculation of the spectroscopic mode in question ω_1 as well as another fundamental mode ω_3.

TZ...	Triple Zeta.
2P...	Double Polarization.
SCF....	Self Consistent Field.
CISD...	Configuration Interaction. Single and Double Excitation.
CCSD...	Coupled Cluster. Single and Double Excitation.
(T)...	Triple Excitations included perturbatively.
+ f...	Also includes f functions on Si and C atoms.
EXT....	Extended Basis Set.

Several features of these results are significant.

(i) The addition of f orbitals on the silicon and carbon atoms, which usually improves agreement with experiment in these types of calculations, produces a worsening in the frequency error in three separate methods (SCF, CI and EXT SCF), although the energy shows improvement.

(ii) None of the above methods emerges as the clear winner in calculating fundmental modes from first principles. The outcome seems to depend on which particular mode is being considered.

(iii) Overall, the error in ω_1 strays considerably from one method to the next and even on going to more extended sets within the same method.

None of this suggests that we have a reliable method which can be applied systematically to a new molecule and finally, no error bars are computed in order to lend reliability to the calculated values. However, there is worse to come! A week or so after the Schaefer and Grev paper was published, Handy, another leading quantum chemist, presented some new results on the same molecule[4]. This author used an alternative approach called the density functional method which does not depend on solving the Schrödinger equation directly and which is becoming increasingly common in theoretical chemistry (Parr, Yang 1989). Handy announced the following results on the Si_2C molecule.

(i) At low levels of approximation the results are consistent with those of Schaefer and Grev above.

(ii) A more extended calculation causes the computed value of ω_1 to change to a lower value.

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(iii) On addition of f functions to the Si and C basis sets, the value of ω_1 goes to 620 cm^{-1}, i.e., close to the discredited observation of 658 cm^{-1}!

This represents a flat contradiction of Schaefer and Grev results, all of whose methods attribute ω_1 to around 840 cm^{-1}. Once again this raises the question of which of the two observed lines should be assigned to the symmetric stretching mode. It should be recalled that this was precisely the question which had motivated the work of Schaefer and Grev. In more general terms, these findings on Si_2C do not say much for the reliability of current quantum chemistry, the claim that "quantum chemistry has come of age" or indeed the claim that chemistry has been reduced to quantum mechanics.

6. Conclusion

To return to the introduction, it will be recalled that the hope of any strict or exact reduction in the special sciences seems to have been abandoned and that all that remains is the possibility of approximate reduction. However, criteria for approximate reduction have not been put forward and the notion remains vague. The proposal here is that we should make use of an early Putnamian characterization of approximation in the context of theories. That is to say, an approximation is such that the relationships postulated by the theory hold not exactly, but with a certain specifiable degree of error.

As I have argued, errors are seldom computed by independent ab inito criteria in any of the calculations in theoretical chemistry which I discuss. Only the Self-Consistent Field calculations provide an upper bound whereas Many-Body Perturbation Theory and Coupled Cluster methods do not. More importantly perhaps, none of these methods computes a lower bound. As was remarked earlier the calculation of the ground state energies of atoms has been achieved to a remarkable degree of accuracy and similarly calculations on small or even medium sized molecules have given encouraging results. However, whether one can draw the conclusion that chemistry has been reduced rather depends on one's criteria of reduction. If we are to define approximate reduction as has been suggested in this paper then it must be concluded that *chemistry is not even approximately reduced to quantum mechanics.* The point I wish to emphasize is that we should not be misled by the apparent quantitative successes achieved and should appreciate the full nature of the approximation procedures employed.

Notes

[1]It should be mentioned that in the *ab initio* approach the values of experimentally determined fundamental constants such as Planck's constant, the velocity of light and the electronic charge are introduced. However, no experimental information on the particular system under investigation is permitted.

[2]Ramsey has made a similar plea in discussing approximations in general (Ramsey, PSA, 1990). I believe that the calculation of upper and lower bounds would provide the criteria which Ramsey seeks.

[3]For a detailed account of all the calculations on the methylene molecule as well as experimental results see Scerri, E.R., 1993, in 'Correspondence, Heuristics and Invariance, Essays in honour of Heinz Post', pp 45-61, eds, S. French, H. Kamminga, Boston Studies in Philosophy of Science, 148, Kluwer, Dordrecht.

[4]Lecture delivered by N.C. Handy, 'New Applications of Quantum Chemistry', Royal Society of Chemistry Symposium, Cambridge, 3rd December, 1992.

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Reduction and Emergence in Chemistry - Two Recent Approches

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Abstract
Two articles on the reduction of chemistry are examined. The first, by McLaughlin, claims that chemistry is reduced to physics and that there is no evidence for emergence or for downward causation between the chemical and the physical level. In a more recent article Le Poidevin maintains that his combinatorial approach provides grounding for the ontological reduction of chemistry and also circumvents some limitations in the physicalist program. In examining the scientific issues that each author has discussed the present author finds some shortcomings in both of these approaches.

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1. Introduction

In recent years there the reduction of chemistry has been discussed in a variety of ways. Many studies have concentrated on inter-theoretical reduction between theories of chemistry and theories of physics (Bunge, 1982; Primas, 1983). Others have discussed the reduction of chemistry in a naturalistic manner, by examining the question of how some typically molecular properties such as bond angles can be deduced from quantum mechanics in an ab initio fashion or whether the periodic system can be similarly deduced from quantum mechanics (Scerri, 2004). More recently a number of authors have turned to discussing the ontological reduction of chemistry (McLaughlin, 1992; Le Poidevin,

2005). The present article examines the claims regarding emergence and the ontological reduction of chemistry in the last two cited articles.

2. McLaughlin on British Emergentism and the relationship of chemistry to physics

Brian McLaughlin has written a frequently cited paper in which he seeks to give an overview of the philosophical school that he dubs 'British Emergentism' which includes the work of J.S. Mill, Bain, Lewes, Morgan and most recently C.D. Broad. I begin with a brief summary of McLaughlin's characterization of these philosophers, especially of C.D. Broad.

Emergentists held, rather uncontroversially, that the natural kinds at each scientific level are wholly composed of kinds of lower levels, and ultimately of kinds of elementary particles. However, they also maintained that,

> Some special science kinds from each special science can be wholly composed of the types of structures of material particles that endow the kinds in question with fundamental causal powers (McLaughlin, 1992, p. 50-51).

These powers were said to 'emerge' from the types of structures in question. One example given repeatedly by the British emergentists was that of chemical elements which have the power to bond to other elements by virtue of their internal microscopic structures. According to the emergentists, when these causal powers operate they bring about the movement of particles. The striking part, as McLaughlin calls it, about the emergentist claim, is that the kinds pertaining to a special science, such as chemistry, are said to have the power to influence microscopic motions of particles in ways that are not anticipated by the laws governing the microscopic particles. Emergentism is thus committed to the possibility of 'downward causation'.

For example, emergentists such as Broad believed that chemical bonding represents an example of emergence and the operation of downward causation. Indeed he went as far as to declare,

> The situation with which we are faced in chemistry...seems to offer the most plausible example of emergent behaviour (Broad, 1925, p. 65).

Broad believed that emergent and mechanistic chemistry (non-emergent chemistry) agree in the following respect,

> That all the different chemical elements are composed of positive and negative electrified particles in different numbers and arrangements; and that these differences of number and arrangement are the only ultimate difference between them (Broad, 1925, p.69).

However, he also stressed that if mechanistic chemistry were true it should be possible to deduce the chemical behavior of any element from the number and arrangement of such particles, without needing to observe a sample of the element in question, which is something that is clearly not the case.

Against this position McLaughlin maintains that the coming of quantum mechanics and the quantum mechanical theory of bonding has rendered these emergentist claims untenable. In fact he is very categorical about the prospects for modern day emergentism.

> It is, I contend, no coincidence that the last major work in the British Emergentist tradition coincided with the advent of quantum mechanics. Quantum mechanics and the various scientific advances made possible are arguably what led to British Emergentism's downfall...quantum mechanical explanations of chemical bonding in terms of electromagneticism [sic], and various advances this made possible in molecular biology and genetics – for example the discovery of the structure of DNA – make the main doctrines of British emergentism, so far as the chemical and the biological are concerned at least, seem enormously implausible. Given the advent of quantum mechanics and these other scientific theories, there seems not a scintilla of evidence that there are emergent

> causal powers or laws in the sense in question... and there seems not a scintilla of evidence that there is downward causation from the psychological, biological and chemical levels (McLaughlin, 1992, p. 54-55).

These anti-emergentist claims can be criticized on several different fronts. Granted that the quantum mechanical theory of bonding that McLaughlin appeals to does, provide a more fundamental account of chemical bonding than the classical, or Lewis, theory. Nevertheless, it does not permit one to predict in advance the behavior of elements or the properties that a compound might have once any two or more elements have combined together. Moreover, it is not as though there was a complete absence of any theoretical understanding of chemical bonding before the quantum theory was introduced. Lewis's theory, whereby covalent bonds occur when elements share pairs of electrons, gave a good account of the bonding in most compounds. Lewis arrived at his theory over a period of time but his crucial realization was that most stable molecules have an even number of electrons, while unstable ones such as nitrogen monoxide (NO) possess an odd number of electrons. Lewis thus naturally assumed that bonding to form stable molecules involved the pairing of electrons in bonds or as lone pairs.

Admittedly the quantum mechanical theory, devised by Heitler, London, Pauling, Millikan and others goes beyond this 'homely picture' of pairs of electrons, mysteriously holding atoms together. However, Lewis' concept of bonds as pairs of electrons is not thereby refuted but rather given a deeper physical mechanism. According to the quantum mechanical account, electrons are regarded as occupying bonding and anti-bonding orbitals. To a first approximation, if the number of bonding electrons exceeds the number of anti-bonding electrons the molecule is predicted to be a stable one.[1] Moreover, the electrons occupy these orbitals, two by two, in pairs. The deeper understanding lies in the fact that the electrons are regarded as spinning in opposite directions within all such pairs. Indeed it is the exchange energy associated with electron spin which accounts quantitatively for the bonding in any compound and it is in this last respect that the quantum mechanical theory goes beyond Lewis's theory.

Linus Pauling, one of the chief architects of the quantum mechanical account of chemical bonding was quick to point out the continuity with Lewis' concept when he wrote the following passage in perhaps his main contribution to the theory of chemical bonding,[2]

> It may be pointed out that this theory is in simple cases entirely equivalent to G.N. Lewis's successful theory of the shared electron pair, advanced in 1916 on the basis of purely chemical evidence. Lewis's electron pair consists now of two electrons which are in identical states except that their spins are opposed (Pauling 1928, 359).

There is another aspect of McLaughlin's above cited passage that is entirely incorrect, namely his claim that the discovery of the structure of DNA owes something to the quantum mechanical theory of bonding. As a matter of fact there is no connection whatsoever between these two developments. All I can think of to explain McLaughlin's statement is that Pauling was involved in both developments.[3] But of course Pauling rather famously failed to find the structure of DNA and was beaten to it by Crick and Watson.

The discovery of the structure of DNA was driven almost entirely by the X-ray diffraction evidence that became available to Crick and Watson, courtesy of Wilkins and Franklin. It did not rest on any quantum mechanical calculations or indeed any insights provided by the theory.[4] It involved model building and cardboard-cut outs of bases. McLaughlin does not say anything whatsoever about pre-quantum mechanical theories of bonding, except to imply that they were completely inadequate. At the same time he suggests that the quantum mechanical theory has provided a complete answer to the question of bonding. Neither of these extreme positions are correct.

It is not clear whether it is the superior quantitative nature of the quantum mechanical theory that McLaughlin is so impressed by, since he does not say. The only argument offered is that the quantum mechanical theory led directly to the elucidation of the structure of DNA and so on. If one separates any implications of the quantum mechanical theory of chemical bonding for the later developments in molecular biology as I

am urging, it raises the question of why McLaughlin believes that quantum mechanics was so overwhelmingly successful in chemistry, to the extent of rendering emergentism about bonding *completely* untenable. McLaughlin offers us no such argument for the superiority of the quantum mechanical account of bonding over the earlier classical theory of Lewis. McLaughlin implies that the quantum mechanical theory provides what the classical theory could not, namely the power to predict how two elements might react together. Or is McLaughlin suggesting that using quantum mechanics we can predict the properties of an element from a knowledge of the number of fundamental particles that its atoms possess?

Unfortunately, as anyone who is aware of the current state of quantum chemistry knows well, neither of these feats are possible. In the case of elements we can predict particular properties perhaps such as ionization energies but not chemical behavior. In the case of compounds what can be achieved is an accurate estimate, and in many cases even predictions, regarding specific properties in the compounds that are known to have formed between the elements in question. Quantum mechanics cannot yet predict what compounds will actually form. Broad's complaint about the inability of mechanistic or classical chemistry to predict the properties of elements, or the outcome of chemical reactions between any two given elements, remains unanswered to this day. Why then should we accept McLaughlin's claim that pioneer quantum chemistry, or even today's version of the theory of bonding, can so decisively deal a death-blow to any notions of emergence and downward causation?

Of course if McLaughlin believes otherwise the onus is on him to marshal some support from the contemporary literature in quantum chemistry. Merely claiming, incorrectly as it happens, that the theory of bonding led to development of molecular biology will simply not do.

In any case, as McLaughlin himself seems to concede, the advent of a quantum mechanical theory of bonding did not in fact kill off emergentism completely since some prominent biologists and neurophysiologists such as Roger Sperry, whom he cites, continued to work in this tradition. Moreover, if one surveys the literature in science as well as philosophy of science, one cannot fail to be struck by the

're-emergence of emergence', as it has aptly been termed (Cunningham, 2001). This is equally true of the humanities as it is of the physical sciences. For example, the prominent Harvard chemist George Whitesides has been showing increasing support for claims for the emergence of chemical phenomena from physical ones, precisely the example of emergence which McLaughlin wishes to deny so strenuously (Whitesides, Ismagilov, 1999). Rather than being 'killed off' by the quantum mechanical account of chemical bonding, emergence is alive and well. McLaughlin's attempt to assert the reduction of chemistry by appealing to the non-existence of emergence of the chemical from the physical, and his associated denial of downward causation are thus entirely unconvincing at least to the present author.

Finally, as Kim has pointed out in another context, the notion of emergence is a perfectly respectable one that bears some striking similarities to the currently popular notion of non-reductive physicalism that prevails in the philosophy of mind.[5] I do not believe that a straightforward appeal to the quantum mechanical account of chemical bonding can be taken as signaling the demise of emergence of chemistry from physics. I suggest that the claim made by McLaughlin takes the Quinean recommendation, of finding one's ontology from contemporary scientific theories, a little too far.

3. Another approach to the Reduction of Chemistry - Le Poidevin

The second article under consideration also raises the question of the ontology of chemistry. To what extent can we avail ourselves of knowledge obtained through theories such as quantum mechanics? Robin Le Poidevin, contrary to McLaughlin's approach, believes that we need to separate ontology from epistemology rather sharply.[6] He claims to have given an argument in favor of the ontological reduction of chemistry, which does not appeal to the fortunes of any particular physical or chemical theory. He also hopes to bypass the kinds of problems that beset a physicalist approach to ontological reduction. As he explains, these problems apply to the reduction of the mental, as much as they do to the reduction of the biological or chemical levels to fundamental physics.

Le Poidevin makes special mention of the periodic system and of Mendeleev's prediction of new elements. He sets out to discover why Mendeleev was so confident that the elements he predicted actually existed. Le Poidevin claims that this is not a question about Mendeleev's confidence in the periodic law but rather about an implicit conceptual move. If one grants that the gaps in the periodic table represented genuine possibilities, elements that could exist, why did Mendeleev assume that the possibilities would actually be realized?

Le Poidevin then draws the following distinction.

> Even if some elements in the table are merely possible, there is a genuine difference between the physical possibility of an element between, say, zinc and arsenic (atomic numbers 30 and 33), and the mere logical possibility of an element between potassium and calcium (19 and 20) (Le Poidevin, 2005, p. 119).

I refer to this passage because the discreteness in the existence of elements goes on to play a pivotal role in Le Poidevin's eventual argument in favor of the ontological reduction of chemistry. Le Poidevin agrees with those who in recent years have claimed that chemistry is not reduced to physics in an epistemological sense but, to repeat, his real goal is to examine the ontological question without appeal to theories.

> The thesis of ontological reduction is that properties we would recognize as paradigmatically falling within the domain of chemistry are determined by more fundamental properties. Ontological reduction is not committed to the view that we are already acquainted with these more fundamental properties, nor even that, once acquainted with them, we could successfully derive the chemical properties from the fundamental ones. There is, I think, a strong intuition that ontological reduction is true, whatever the fortunes of epistemological reduction. But what is the source of this intuition? Can ontological reduction be defended independently of epistemological reduction? (Le Poidevin, 2005, p. 120-121).

Le Poidevin's answer to the last question is that it can. In addition he is well aware that the frequent appeal to physicalism that is made, especially in the philosophy of mind, is plagued by some rather serious problems. The author reminds us that the claim that chemical properties supervene on those properties described by the supposedly complete science is just as trivial as the thesis that mental properties do. Secondly he brings up the so-called 'symmetry problem'. Even if we suppose a one-to-one correspondence between a given chemical property and one described by physics, that correspondence would not by itself suggest that one is more fundamental than the other

Le Poidevin considers the relationship between valence and electronic configuration in an effort to cast further light on these issues,

> Suppose, for example, valency to supervene on electronic configuration. At first sight, the relation appears to be asymmetric because of a valency of 1, for example, can be realized by a number of distinct configurations, but nothing can differ in terms of valency without also differing in terms of electronic configuration. However, the relevant part of the configuration--the part that determines valency--will not vary among elements of the same valency. The determination therefore goes both ways (Mumford [1994]). So chemical reductionism, the one thing that physicalists supposed they could hold up to the world as a shining example of the success of their programme, is suspect for some of the same reason that physicalism about the mental is suspect (Le Poidevin, 2005, p. 123-124).

Is Le Poidevin correct in his assertion that " nothing can differ in terms of valency without also differing in terms of electronic configuration"? In fact this is not the case since, as is well known, most non-metal elements can show variable valences in spite of possessing a single electronic configuration. Sulfur, to take just one example, has the electronic configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^4$. Nevertheless, it commonly shows valences of +2, +4 or +6 such as in the compounds SCl_2, SO_2 and SO_3 respectively.

But Le Poidevin is nevertheless correct in pointing out that in general the symmetry problem is a pressing one. One cannot be sure that it is the 'lower' levels that determine the 'upper' levels and not vice versa. The grounding of reduction requires something more than the physicalist prejudice, or the hope, that physical levels determine chemical levels and not vice versa. Le Poidevin propose to circumvent both this problem and the problem of vacuity, mentioned above, by an approach that he terms combinatorialism.

> The central contention of combinatorialism is this: possibilities are just combinations of actually existing simple items (individuals, properties, relations). Let us call this the *principle of recombination*. To illustrate it, suppose the actual world to contain just two individuals, a and b, and two monadic properties, F and G, such that (Fa & Gb). Assuming F and G to be incompatible properties, and ignoring the possibility of there being nothing at all, then the following is an exhaustive list of the other possibilities:
>
> 1. Fa
> 2. Fb
> 3. Ga
> 4. Gb
> 5. Fa & Fb
> 6. Ga & Gb
> 7. Ga & Fb
>
> (Le Poidevin, 2005, p. 124).

Le Poidevin explains that combinatorialism is a form of reductionism about *possibilia*. He claims that the talk of non-existent *possibilia* is made true by virtue of actual objects and their properties, just as the inhabitants of his model world are made possible by virtue of a and b and the properties F and G. The idea is that we should consider Mendeleev's predicted elements in this way. According to Le Poidevin's approach, the elements that are as yet non-existent but physically

possible are those that can be regarded as combinations of some undefined basic objects and/or basic properties.

Le Poidevin suggests that this approach provides a means of establishing the required asymmetry in order to ground the reduction of the chemical to the physical or the mental to the physical, and a means of countering the symmetry problem alluded to earlier.

> A property-type F is ontologically reducible to a more fundamental property-type G is the possibility of something's being F is constituted by a recombination of actual instances of G, but the possibility of something's being G is not constituted by a recombination of actual instances of F (Le Poidevin, 2005, p. 129).

I come now to the crucial argument in Le Poidevin's paper,

> But since the thesis of ontological reduction is about properties, we do have to have a clear conception of what is to count as a chemical property. I shall take the identity of an element, as defined by its position in a periodic ordering, and its associated macroscopic properties (capacity to form compounds of a given composition with other elements, solubility etc.) to be paradigmatically chemical properties. About these properties we can be unapologetic realists. A periodic ordering is a classification rather than a theory, so this conception of chemical properties is as theory-neutral as it can be.[7] Below this level, the theoretical content, and corresponding pressure to be instrumentalist, increases. The question of the ontological reduction of chemistry (or at least the question I am interested in) is the question of whether these paradigmatically chemical properties reduce to more fundamental properties (Le Poidevin, 2005, p. 131).

Let me say something about the second sentence since I think this will turn out to be Le Poidevin's undoing. In his brief list of what he terms paradigmatically chemical properties the author has lumped

together (a) the identity of elements, (b) their capacity to form compounds of a certain composition and (c) their solubilities. But there is a long-standing philosophical view whereby elements should be regarded as having a dual nature consisting of basic substances and of simple substances (Paneth, 1962). If one takes this dual view seriously it casts doubt on Le Poidevin's lumping together of the existence of elements and their properties such as solubilities.

As Mendeleev, and more recently Paneth among others have stressed, the notion of an element as a basic substance concerns just its identity and its ability to act as the bearer of properties. A basic substance does not however possess any properties.[8] The 'properties' of an element however reside in the simple substance and not in the element as a basic substance. According to this view, the identity of an element and its properties are regarded as being quite separate. If we consider le Poidevin's three examples, namely identity, capacity to form compounds and solubility we see a conflation of basic substance aspects (identity) with simple substance aspects (solubility). It is only by failing to distinguish between the identity of elements and their possessing properties, such as solubility, that Le Poidevin is able to give the impression that he has provided an argument for the ontological reduction of chemistry as a whole.

He then adds,

> We might, just accept it as a brute fact about the world that the series of elements was discrete. But if there were a finite number of properties, combinations of which generate the physical possibilities represented by the periodic table, then variation would necessarily be discrete rather than continuous. We can believe in the existence of these fundamental entities and properties without subscribing to any particular account of them (e.g. an account in terms of electronic configuration), such accounts at least show us the way in which chemical properties could be determined by more fundamental ones. The point is that, given the principle of recombination, unless those more fundamental properties exist, unactualized elements would not be physical possibilities (Le Poidevin, 2005, p. 131-132).

Let me try to rephrase the argument. We assume that the combination of a finite number of fundamental properties, via a combinatorial approach, leads to a discrete set of macroscopic physical possibilities. We also know empirically that the chemical elements occur in a discrete manner since there are no intermediate elements between, say, hydrogen and helium. Le Poidevin is thus claiming that his combinatorial approach can be taken as an explanation for the discreteness in the occurrence of elements and furthermore that it justifies the fact that Mendeleev regarded the yet undiscovered elements like gallium as being physical possibilities rather than merely logical ones.

4. Further comments on Le Poidevin

One might even grant that Le Poidevin's argument provides the sought after justification for the ontological reduction of the chemical elements to fundamental physical properties. But has Le Poidevin provided any grounding for the ontological reduction of chemistry *tout court*? I think not. For example, the solubilities of elements which the author included in his list of paradigmatically chemical properties does not occur in a discrete manner. A particular ionic compound can have a solubility of 5 grams per liter. Another one might have a solubility of 6 grams per liter of water. But there is nothing discrete about solubility. It is quite possible that other salts will display solubilities falling *anywhere* between these two values.

Unlike the existence of chemical elements which does appear to be a discrete phenomenon, solubility or acidity or basicity or oxidizing power or indeed almost every "paradigmatically chemical property" does not form a discrete set. As a result one cannot invoke a combinatorial argument of the type suggested by Le Poidevin in order to provide an ontological grounding for these properties. Le Poidevin would only have provided a general argument for the ontological reduction of chemical properties in terms of combinatorialism if all properties, without fail, displayed discreteness in the manner in which they occur.

As to whether Le Poidevin has separated the question of ontological reduction as fully from that of epistemological reduction as he seemed to promise in his article, I have some doubts. Admittedly, the

ordering of the chemical elements may not be in any sense theoretical, as he states, but there is no denying that ordering the elements by way of atomic number, or by whatever other means, is dependent on our *knowledge* of the elements. It is just that this knowledge takes the form of a classification or ordering rather than a theory as Le Poidevin correctly points out. But surely this does not render the act of classification any less epistemological.

Finally, I would like to point out some specific points concerning Le Poidevin's analysis. Let me return to the question of the discrete manner in which the elements occur. Le Poidevin takes this fact to support a combinatorial argument whereby a finite number of fundamental entities combine together to give a discrete set of composite elements. But what if we consider the combination of quarks (charge = 1/3), instead of protons (charge = 1)? In the former case a finite number of quarks would also produce a discrete set of atoms of the elements only the discreteness would involve increments of one-third instead of integral units. In fact chemists and physicists have been actively searching for such 'quark matter' (Jørgensen, 1982)

And if this matter were found, it would then be physically possible for there to be two elements between say Z = 19 and Z = 20 to use Le Poidevin's example. Let us further suppose that a future theory might hold that the fundamental particles are some form of sub-quarks with a charge of 0.1 units. Under these conditions combinatorialism would lead to the existence of nine physical possibilities between elements 19 and 20, and so on. It would appear that Le Poidevin's distinction between a physical possibility, as opposed to a merely logical one, is dependent on the state of knowledge of fundamental particles at any particular epoch in the history of science which is surely not what Le Poidevin intends. Indeed the distinction proposed by Le Poidevin would appear to be susceptible to a form of vacuity, not altogether unlike the vacuity which is faced by physicalism, and which was supposed to be circumvented by appeal to combinatorialism.

Finally there is a somewhat general objection to the use of combinatorialism in order to ground the ontological reduction of chemistry. It would seem, at least to the present author, that the assumption that fundamental entities combine together to form

macroscopic chemical entities ensures from the start that the hoped for asymmetry is present. But it seems to do so in a circular manner. If one assumes that macroscopic chemical entities like elements are comprised of sub-atomic particles then of course it follows that the reverse is not true. The hoped for asymmetry appears to have been written directly into the account, rather than deduced.

5. Conclusion

After many years during which philosophers of chemistry concentrated on the question of the epistemological reduction of chemistry, and had perhaps dismissed the question of ontological reduction as a foregone conclusion, there has been a recent resurgence of interest in the ontological question. McLaughlin has used the success of the quantum theory of chemical bonding to conclude *incorrectly* that the emergence of chemistry from physics is entirely ruled out. Le Poidevin claims to have given an ontological argument in favor of the reduction of chemistry which does not appeal to any physical theories and yet it appears to do just that.

My own conclusion is that one should exercise moderation between an extreme Quinean approach of attending mainly to scientific theories and Le Poidevin's approach of dispensing altogether with the findings of scientific theories. Surely a more subtle approach is required in trying to uncover the ontology of chemistry or any other special science. Of course one needs to consult the findings of the empirical sciences in question, but there is still scope for philosophical consideration, perhaps along the general lines offered by Le Poidevin. Philosophical positions such as reductionism, atomism and emergence cannot be judged only on the basis of some contemporary theory or other. In addition if one does consult the findings of scientific theories to draw ontological lessons it is essential for one to do so in an accurate manner and not in the way that these two authors appear to have done.

It is encouraging to see mainstream philosophers now taking an interest in chemistry. But surely they also need to get the chemistry right.

NOTES

[1] I am referring here to molecular orbital theory as developed by Mulliuken, Hund and others which is mathematically equivalent to the valence bond method to which Pauling made seminal contributions. The notion of bonds as pairs of electrons is no less retained in the valence bond method which in many senses is closer to Lewis' classical theory, although I do not have the space to enter into the details here.

[2] This article is singled out, and reproduced, in a recent book by Alan Lightman as one of the 22 most influential scientific articles of the twentieth century. (Lightman, 2005).

[3] Admittedly Pauling discovered that protein molecules have the structure of an α helix and this was a step towards the realization by Crick and Watson that DNA has a double helical structure. But no quantum mechanics went into Pauling's discovery. Furthermore, Pauling was involved in the race to find the structure of DNA but by his own admission was working on altogether the wrong track. Neither he nor Crick and Watson employed any quantum mechanics in their search for the structure of DNA. McLaughlin repeats his false claim again, regarding the path to the discovery of the structure of DNA, later in the article.

[4] Among the other evidence was a knowledge of base pairing which had been obtained previously by Chargaff. The definitive source on the discovery of the structure of DNA is due to Robert Olby, 1974.

[5] This is not to say that Kim supports either emergence or non-reductive physicalism. In fact he argues that non-reductive physicalism in particular represents an unstable position (Kim, 1999).

[6] In this respect Le Poidevin differs from other contemporary authors whose ontological views are heavily influenced by theoretical developments in quantum chemistry (McLaughlin, 1992).

[7] It may well be theory neutral but it is surely not epistemologically neutral. God does not order the elements. It is scientific knowledge by way of Moseley and others that has allowed us to order the elements into

a coherent sequence. Again I don't want to deflect any attention from the main line of argumentation.

[8] Except for possessing an atomic weight which is the characteristic property of an element as a basic substance for Mendeleev. In modern terms, the characteristic property becomes atomic number.

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Section B

The Periodic Table, Electronic Configurations and the Nature of the Elements

ERIC R. SCERRI

HAS THE PERIODIC TABLE BEEN SUCCESSFULLY AXIOMATIZED?

ABSTRACT. Although the periodic system of elements is central to the study of chemistry and has been influential in the development of quantum theory and quantum mechanics, its study has been largely neglected in philosophy of science. The present article is a detailed criticism of one notable exception, an attempt by Hettema and Kuipers to axiomatize the periodic table and to discuss the reduction of chemistry in this context.

1. HISTORICAL PRELUDE AND THE TREATMENT OF THE PERIODIC SYSTEM AND TABLE IN THE PHILOSOPHICAL LITERATURE

The Periodic Table of the elements has had a profound influence on the development of modern chemistry and physics. In chemistry its influence is well known and undeniable. The periodic system functions as a unifying principle which continues to guide the day-to-day research of chemists in many specialized areas. The influence of the periodic table on the development of physics and in particular quantum mechanics is not so well known but equally undeniable.

Shortly after the turn of the century, J. J. Thomson, the discoverer of the electron, regarded the question of trying to explain the periodic table through atomic physics as one of the major unsolved problems. In 1904 he tried to account for the periodicity of the elements in terms of the arrangement of electrons in rings. Thomson proposed a detailed set of atomic configurations as part of his plumb pudding model in which electrons were embedded in the main body of the atoms and were held to circulate in concentric rings (Thomson, 1904).

The particular arrangement of how many electrons should occur in each ring was adapted from the earlier work of an American physicist Mayer, who had experimented by floating small bar-magnets inside a circular basin of water and observed that stable rings required a particular number of magnets (Mayer, 1878). Although Thomson's tables of electron rings do not show the periodicities at the atomic numbers which we now know them to occur at, it must be remembered that there was still a good deal of confusion as to the numbers of electrons contained by atoms of even low

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atomic weights at this time.[1] Thomson merely showed the plausibility of explaining chemical periodicity by similarities in electronic configurations among atoms of different elements.

Soon afterwards, Thomson's atomic model was deposed in favor of Rutherford's nuclear atom in which the electrons were considered to orbit the small central nucleus. This task was achieved, partly, by Niels Bohr while on his postdoctoral year in Cambridge and Manchester following the completion of a PhD in Copenhagen.

It has been persuasively argued that Bohr was initially concerned with trying to obtain the electronic configurations of the atoms in the periodic table and that only later did his attention turn to the spectrum of hydrogen, for which he seems to be better remembered, especially by physicists (Heilbron and Kuhn, 1969). Indeed, the first time that Bohr introduced the famous condition for the quantization of electron energy it was in the context of examining Thomson's model of electron rings.[2] Bohr was clearly driven by the desire to understand the periodic table of the elements and devoted many articles to postulating electronic configurations for all the known elements as well as elements which had not yet been discovered.

Although Bohr's old quantum theory was initially successful, various technical problems arose including that of the anomalous Zeeman effect which was to exercise the most brilliant physicists of the day. Wolfgang Pauli eventually solved this problem by postulating that electrons possessed a fourth degree of freedom in addition to the three which had been discovered up to that point. Armed with this new quantum number, Pauli then attacked, what he too regarded as a major question, that of the structure of the periodic table. More specifically his motivation was to try to settle the question of the closing of the electron shells, that is to say the varying lengths of successive periods in the table. This was the context in which Pauli discovered the Exclusion Principle which stipulated that no two electrons could share the same four quantum numbers. When this recipe was added to the already established relationship between the previously known three quantum numbers possessed by each electron, the length of successive periods in periodic table emerged in a completely natural manner (Pauli, 1925).

The old quantum theory was eventually found to possess so many problems that it required a major re-formulation on the part of Schrödinger and Heisenberg, whose equivalent but distinct approaches provided a way out of the 'impasse' through quantum mechanics. However, the Pauli principle, regarded as a bridge between the old and the new quantum theories, was retained, albeit in a modified fashion. The reformulation of Pauli's principle called for an abandonment of the notion of stationary states for

individual electrons.[3] Only the atom as a whole could be regarded as possessing stationary states. In the Schrödinger treatment the wavefunction for the system of electrons would be described by a wavefunction which is anti-symmetrical with respect to the interchange of any two electrons, a result which was independently established by Heisenberg and Dirac (Heisenberg, 1925; Dirac, 1926).

In spite of the central role played by the periodic table its importance seems to have been overlooked in the literature on philosophy of science. Indeed there is only a single paper, to the best of the authors knowledge, which is dedicated entirely to the nature of the periodic table (Hettema, Kuipers, 1988). In addition to this contribution there are a handful of articles in edited collections which deal with certain aspects of the periodic table and periodic law.[4]

However, in view of the interest on the nature of scientific laws in contemporary philosophy of science, (Armstrong, 1988; Dretske, 1977; Lang, 1993; Tooley, 1977; Woodward, 1992), it is somewhat surprising that no major study[5] has been conducted on the law-likeness or otherwise of the so-called periodic law which is embodied in the periodic table.

2. HETTEMA AND KUIPER'S ATTEMPT TO AXIOMATIZE THE PERIODIC TABLE

As mentioned above, there has been one single work entirely dedicated to the nature of the periodic table. Kuipers and Hettema have attempted to obtain an axiomatization of the periodic system and in the process, claim to have answered the question of whether chemistry is reduced to atomic theory.

I will return to the question of axiomatization and reduction later in this paper, but first I examine a number of statements and claims made by these authors in their introduction. [my numbering];[6]

1. "We obtain a naive and a sophisticated version of the Periodic Law and hence of the Periodic Table" (p. 387)
2. "It is claimed [meaning the authors claim] that the physicist and the chemist have a different conception of the atom, that the original version of the Periodic Table is based on the chemist's conception, and that the conception of the physicist, based on the Atomic Theory, has gradually taken its place". (p. 387)
3. "... Atomic Theory can explain (and even reduce) the chemist's formulation of the sophisticated Periodic Law". (p. 387)

4. "... we discuss ... whether the Periodic Table is a proper theory or merely an empirical law". (p. 390)

Claim 1 is based on the notion that the periodic table began as a law of octaves, in other words it was first believed that the repetition in the properties of the chemical elements would occur after an interval of eight elements. This view is attributed by the authors to Mendeleev, the Russian chemist who is generally credited with the discovery of the Periodic Law.

According to Mendeleev, there is a unique periodicity, namely 8 (if we include the inert gases): the 8th element, according to the mass-sequence, before or after a given one is similar to that given one. In terms of atomic numbers Mendeleev's Periodic Law, to be called the naive Periodic Law (NPL), can be formulated as follows

NPL $e \sim e'$ iff $|z(e) - z(e')|$ is a multiple of 8.[7] (p. 396)

In fact, at no point in the evolution of Mendeleev's periodic tables, over half of which were published,[8] did Mendeleev ever adopt such a view (van Spronsen, 1969). If one considers the group of alkali metals, for example, and one asks the question of how many elements occur before the repetition of another alkali metal, Mendeleev's most frequently quoted periodic table of 1871 shows a sequence of 7, 7, 17 and 17 .... If one includes the noble gases then Mendeleev's tables would give intervals of 8, 8, 18, 18 ....[9]

Quite apart from any historical inaccuracy, this is a serious error on the part of the authors since they make this feature, of strict octaves as opposed to varying periodicity, the all-important distinction between what they call the naive and the sophisticated version of the Periodic Table.[10]

SPL ... [sophisticated Periodic Law] states and hence predicts that similarity implies that the respective atomic numbers differ some instance of $2n^2$ (2, 8, 18, 32 ...) ... (p. 397)

A similar claim is made in the following paragraph,

SPL ... states and hence predicts that there is always a similar element at a distance of some instance $2n^2$ after/before a given element if there is a similar one after/before at all. (p. 397)

These claims on the length of the varying periodicities are also incorrect. The repetition of the elements follows the sequence 2, 8, 8, 18, 18, 32 ... as opposed to the authors statement that it is 2, 8, 18, 32. The formula of $2n^2$ which is cited by Hettema and Kuipers refers to the maximum number of electrons which successive shells can accommodate. However, the sequence in which electron shells are filled is complicated by the fact that not all shells are filled completely before a new shell is begun (Löwdin, 1969).[11] This feature, which is ignored by the formula which Hettema and

Kuipers appeal to, gives rise to the transition and inner transition series of elements and hence the characteristic form of the modern periodic table.

This false distinction made by Hettema and Kuipers is one of several, as will be argued, which serve to cause confusion regarding the claims which they make following their axiomatization of the Periodic Table. If there is any sense in which one may distinguish between a naive and a sophisticated version of the periodic table, it lies with the use of atomic weight and later the property of atomic number to order the elements. Whereas atomic weight was first used by the likes of Mendeleev, Newlands and all other pioneers of the periodic table, the subsequent and more fundamental ordering principle is based upon atomic number or number of protons in any atom, following the work of Moseley (Moseley, 1913). Although Hettema and Kuipers show that they are aware of this transition they do not seem to attribute the appropriate significance to it.

In claim 2 the authors express the view that physicists and chemists have a different conception of the atom. It is not clear whether they intend this as a historical claim, which would be correct at a certain epoch of the development of chemistry and physics, or whether they imply, incorrectly, that this is the current view. Later in paper it becomes clear that they do in fact intend this distinction to hold for contemporary chemistry and physics.[12]

In claim 3 it is not clear what Hettema and Kuipers take to be "atomic theory". Do they take it to mean the ordering of the table according to atomic number instead of atomic weight? Do they take it to mean Thomson's atomic theory which, as mentioned in the introduction, represented an early attempt to 'reduce' the periodic table? Do they intend atomic theory to be identified with Bohr's theory which provided a deeper explanation of the Periodic Table? Finally, and this is surely the sense which should be attached to the phrase 'atomic theory', are the authors referring to the new quantum mechanics of Heisenberg and Schrödinger?[13] When the question of the reduction of chemistry is discussed by philosophers it is usually whether chemistry is reduced to this more mature theory of quantum mechanics (Primas, 1983; Liegener, Del Re, 1987; Scerri, 1994a).

Turning to claim 4, the authors ask whether the periodic table is a proper theory or merely an empirical law. I believe that this statement represents a category mistake. The periodic table itself is neither a theory nor a law. There is no such thing as *the* periodic table. The mere fact that over 700 periodic tables have been produced shows that the representation of the periodic law is rather arbitrary (Mazurs, 1974). What is important is the statement of the periodic law which any periodic table attempts to

represent graphically. I delay a discussion of the main substance of this claim regarding the status of the periodic law.

The following section Hettema and Kuiper's article consists of a brief and generally accurate account of the early historical development of the periodic table. The only important omission would seem to be the author's failure to mention the experimental work of Henry Moseley, in 1913, which established that the correct ordering principle for the elements consists in atomic number instead of a atomic weight. This development is crucial for the arguments contained in Hettema and Kuipers' article, since they go on to discuss whether the ordering number z (implicit in the work of Mendeleev but explicit in the modern table) is or is not a theoretical quantity. In the course of this discussion the authors suggest that the change in the ordering principle from atomic weight to atomic number is somehow not accessible to experiments.[14]

Moseley initially conducted his experiments on twelve elements, ten of which occupied consecutive places in the periodic table. He thus discovered that a plot of the frequency of the so-called K lines in the spectrum of each element was directly proportional to the square of an integer representing the position of each element in the periodic table. This result suggested that there is a fundamental quantity in the atom which increases by regular steps as we pass from one element to the next. This quantity was subsequently referred to as the atomic number of an element and eventually identified with the number of protons contained in the nucleus of any particular atom. Moseley's discovery shows unambiguously, that tellurium should be placed before iodine in the periodic table, which is in keeping with the chemical behavior of these elements. The atomic weight ordering which holds that iodine should be placed before tellurium is thereby refuted, as it is in the case of the other pair reversals in the periodic table.[15]

In section 3 Hettema and Kuipers begin their main task of axiomatizing the periodic table. In order to construct a "potential model" for the periodic table the authors depart from the historical development, as one might rightly expect in any attempted axiomatization. The potential model which is to serve to axiomatize the early periodic table as well as the modern version includes both atomic weight and an atomic number function, z. To justify such an approach the authors state that Mendeleev implicitly realized the need to use z,

Mendeleev did not explicitly introduce atomic numbers, but in developing the two-dimensional table, starting from the atomic mass sequence, he left open spaces for not yet discovered elements, just on the basis of his idea that there is a period of 8 elements. Of course in this way he introduced implicitly the atomic numbers. (p. 396)

Whether Mendeleev did implicitly introduce atomic numbers is debatable. It would seem that the above statement rests on the false assumption that Mendeleev was in favor of a constant periodicity of eight elements.[16]

After stating the definition for a potential model the authors explain how their terms m and $\sim$ can be determined experimentally and that z is the only "theoretical term" of the five terms discussed. Now admittedly Mendeleev could not determine z experimentally and so for him it would indeed have been a theoretical term. Howeve-, for the modern periodic table z is no longer merely theoretical, since it can be measured via Moseley's experiment, a fact which pre-dates the important developments in atomic theory of Bohr, Pauli, Schrödinger and so on. For the periodic table "based on atomic theory", as the authors would have it, it must be concluded, contrary to Hettema and Kuipers, that z is not in fact a theoretical term.

On page 395 the authors take up their claim to discussing two versions of the periodic table as mentioned in the introduction. Once again, they claim that the latter was developed "in contact with atomic theory". As mentioned above, if there is any sense in which one can distinguish between a naive and sophisticated form of the table it would be to call Moseley's version sophisticated. All subsequent developments in atomic theory merely serve to represent, in the sense of presenting again, the periodic table in terms of atomic structure but fail to bring to it any fundamental changes as has been argued elsewhere (Scerri, 1994b).

Another distinction made by Hettema and Kuipers consists in the difference between what they term the chemical atom and the physical atom. However, the way in which they choose to draw such a distinction is somewhat vague.

> In chemistry nowadays there exists a tendency to base qualitative discussions on a highly approximate level of the physical picture of the atom. (In fact, the level of approximation can become so high, that this kind of picture cannot be called 'physical' any longer.) (p. 400)

Are the authors perhaps referring to the electronic configurations of atoms at this point? If so, it is not clear at what point this model can be said to cease to be physical as they suggest. After all, atomic physicists make ample use of electronic configurations of atoms, as do chemists.

Hettema and Kuipers further claim that the

> ... obtained results, as they emerge out of these qualitative discussions concern mainly molecular properties. (p. 400)

In fact one of the main purposes in using electronic configurations lies in the calculation of ground state energies, a feature which applies equally well

to atoms as it does to molecules. Indeed, the basis sets used in molecular calculations depend on the prior calculation of atomic basis sets. The authors then attempt a more precise explanation of the difference between the chemical and the physical atom and in doing so commit another fallacy.

> ... a 'chemical' conception distinguishes itself from the 'physical' picture by being primarily meant to describe the role atoms play in molecules. (p. 401)

Unfortunately this interpretation does not leave room for a discussion of the chemistry of atoms or in other words for the attempt to reduce the periodic table of the elements to quantum mechanics[17] or atomic theory, which is a question that Hettema and Kuipers claim to discuss in their article. The authors continue by saying,

> ... In the 'chemical' picture of the atom for instance, 'chemical similarity', includes 'having the same valency' while in the 'physical' picture, 'chemical similarity' can be related to similarities in the 'outer electron configuration' (This means automatically that also the concept of 'valency' itself can be related to 'outer electron configuration'.') (p. 401)

In fact the concept of electronic configuration as a causally explanatory feature has become very much the domain of chemistry or to be more precise it is *the* dominant paradigm in modern chemistry. Conversely, physicists are only too aware of the limitations of the electronic configuration model and they only draw upon it as a zero order approximation. Hettema and Kuipers further state that Bohr's theory of the atom, despite its level of approximation, is to be regarded as a physical theory because the explanation of the periodic table was only a spin-off from its development. But given Heilbron and Kuhn's detailed version of the historical development, it was precisely the explanation of the periodic table which provided the initial impetus for Bohr's famous theory of the atom, whereas the explanation of the hydrogen spectrum only arose later. (Heilbron and Kuhn, 1969).

According to Hettema and Kuipers,

> ... the relation $\sim$ now indicates [in the sophisticated periodic table] the relation of having the same 'valence electron configuration', this means that two elements stand in the relation $\sim$ e.g., when both have a d^3 configuration. All groups, occurring in the Periodic Table, can be identified with some sort of 'outer electron configuration'. (p. 402)

This statement is factually incorrect. The possession of a particular outer electron configuration is neither a necessary nor sufficient condition for membership of any particular group in the periodic table. To make matters even worse, the example of a d^3 configuration given by Hettema and Kuipers is rather unfortunate since of the three elements vanadium, niobium

and tantalum which belong to group 15 of the periodic table,[18] by virtue of their very similar chemical properties, only vanadium and tantalum have an electronic configuration which includes d^3.[19] This example among many others[20] shows that the possession of a particular electronic configuration is not a necessary condition for the display of any characteristic chemical behavior. Similarly, examples may be cited to show that the possession of a particular configuration is not sufficient for the possession of a particular chemical property. The elements helium, beryllium and magnesium, for example, all share an outer shell configuration of s^2 and yet helium is a highly inert gas which is invariably placed at the head of the noble gases while beryllium and magnesium are reactive metals which belong in the alkaline earth group of the periodic table.

In a section entitled "A case of reduction", the authors conclude that the sophisticated periodic table can be explained using atomic theory. The basis for this conclusion is the authors view that the term z can be identified with the number of electrons in any neutral atom. They state that,

> The necessary link between chemical similarity and equal outer electron configuration states that the latter causes the former. (p. 403)

It is interesting to contrast the above statement with that of one of the leading authorities on electronic configurations of atoms,

> No simple relation exists between the electron configuration of the ground state of the atom and the chemistry of the element under consideration. (Jørgensen, 1973).

Moreover, a reduction of chemistry, or more specifically the periodic table, to quantum mechanics requires far more than a mere approximate explanation of the properties of elements in terms of outer electron configurations. After all, quantum mechanics or "atomic theory", which the authors constantly allude to, is not a qualitative theory dealing in outer-shell electrons. Such explanations are indeed frowned upon by physicists as being of a typically picturesque and naively realistic kind, typical of chemists. Worse still, according to quantum mechanics, the very notion of electron shells or electron configurations becomes strictly invalid as mentioned in the introduction.[21]

Nevertheless, the connection between chemical behavior and electronic configurations can be improved by approaches practiced in computational quantum chemistry. Calculations generally consist in expanding the wave-function of a many-electron atom, for example, as a linear combination of terms representing excited state configurations, in addition to the ground state configuration. A more realistic approximation to chemical behavior of atoms is thus achieved through a superposition of numerous, often

thousands, of configurations and not merely the ground state configuration which features exclusively in the qualitative explanation of the periodic system.

Finally, on the basis of their axiomatization, Hettema and Kuipers make the interesting proposal that whereas the periodic table represents a proper theory for Mendeleev, it is an empirical law from the perspective of atomic theory. Although this overall conclusion is partly correct, I believe that the authors arrive at it for the wrong reason. The notion that the periodic table has been reduced by the understanding provided by quantum mechanics is one that is generally held. Of course the degree to which the periodic table has been reduced can be disputed, but most authors favor the view that an approximate reduction of the table has indeed been achieved.[22]

For example, the calculation of the total energy of each atom, a property which shows marked periodicity has been achieved to within 10^{-3} of one percent for many atoms. The situation is somewhat more complicated in the case of atoms with large atomic numbers due to the increasing importance of relativistic effects (Pyykkö, 1978).

The point is, that it does not require an axiomatization of the periodic table to reach this conclusion. Indeed, one cannot help thinking that the axiomatization of Hettema and Kuipers serves to accommodate this generally held belief that the periodic table, or more generally chemistry, can be approximately reduced to quantum mechanics. As is frequently the case with any accommodation of already known facts, there remains the suspicion that the theoretical scheme may have been designed with the end in view, perhaps inadvertently. The claimed axiomatization does not predict anything new about the periodic table which is not already known. Furthermore, the promise of precision which such a formal approach could offer, in principle, is lost because of a compensating imprecision in specifying what is intended by the term "atomic theory". The conclusion that the modern periodic table is not a theory is, likewise, not a new finding. As the authors themselves state, "most books on the subject of practical chemistry" do not treat the periodic table as a theory. Similarly, the philosopher Shapere has taken the view that the periodic table is not a theory but an 'ordered domain' despite the excellent predictive power which it provides.

I now turn to the question of a "proper theory" which Hettema and Kuipers have formalized. The gist of their argument is that proper theories have proper theoretical terms whereas an empirical law lacks such terms.

> Our claim is that z is a proper theoretical function in NPT [Naive Periodic Table] and hence that NPT is a proper theory. (p. 405)

> However, SPL, and hence SPT, were formulated along with the development of AT [atomic

theory], where the atomic number function z obtained the interpretation of the number of electrons.[23] (p. 406)

With some plausible definitions we have arrived at the conclusion that it was a proper theory for Mendeleev, and that (the sophisticated version of) the Table became only an empirical law due to the Atomic Theory. (p. 406)

What is clear however is that the Periodic Table is a nice example of a theory which starts as a proper theory which turns at least *de jure* into an empirical law by underpinning it with another ... (p. 407)

Had Hettema and Kuipers investigated the status of the early periodic tables of Mendeleev and others they would have discovered that at no time has the periodic table ever been regarded as a theory. This point is relevant, even within the authors framework, given that Hettema and Kuipers do not seem averse to considering scientific practice in deciding whether the current table is a theory or not.

Furthermore, the mere presence of a single implicit theoretical term within the periodic law does not appear to provide sufficient grounds for the claim that the naive periodic law should be regarded in hindsight as a theory. The periodic systems, both naive and sophisticated, are systems of classification which are devoid of theoretical status in much the same way as the Linnean system of biological classification or the Dewey decimal system of library classification. None of these systems can be regarded as theories since they do not seek to explain the facts but merely to classify them. However, the fact that the periodic system, even in its early stages, was capable of predicting unknown elements such as germanium, in addition to accommodating the properties of all the known elements, suggests that it constitutes a more natural system of classification than systems used to classify library books for example.

Finally, it should be pointed out that any discussion of reducing the periodic table to electronic configurations falls somewhat short of the mark, since the aim should be to reduce electronic configurations themselves to quantum mechanics. However, as Rouvray among others have recently emphasized, electronic configurations are not reduced to quantum mechanics nor can they be derived from any other theoretical approach. They are obtained instead by a mixture of spectroscopic observations and semi-empirical methods like Bohr's aufbau scheme (Rouvray, 1996; Scerri, 1994b; Scerri, 1997).

To conclude, I believe that the periodic table of elements has yet to be axiomatized successfully, although the bold attempt by Hettema and Kuipers has raised a number of key issues in the philosophy of chemistry.

NOTES

[1] For example, Thomson believed that the atom of oxygen should contain sixty-five electrons rather than the currently accepted value of eight.

[2] The issue is treated in detail by Heilbron and Kuhn and will not be rehearsed here. See especially pp. 245–248 of their 1969 article. The confusion regarding the supposed primacy of the work on the spectrum of hydrogen stems partly from the order of presentation in Bohr's famous 'trilogy' paper of 1913. Section I deals with the hydrogen spectrum, while sections II and III deal respectively with understanding periodicity through electronic configurations and the structure of molecules.

[3] This result has profound implications for the analysis given in later sections of the present article.

[4] Shapere, 1974; Christie, 1994.

[5] Both articles mentioned in note 4 touch on this question.

[6] In their introduction the authors also say,

For the purposes of easy consultation we include here an example of the Periodic Table. We have chosen for the table in Holton (1973). It is not very modern but for this reason it will look familiar not only to chemists but also to readers with only elementary knowledge of chemistry. (p. 390)

In fact, their choice is not only a very unusual version of the table but would definitely not be the version "most familiar to chemists or those with only an elementary knowledge of the subject" as the authors state. For professional chemists, students of chemistry and casual observers alike, the most familiar form of the periodic table, by far, is the medium-long form which has been in standard use since the 1950's and which the authors repeatedly refer to as the sophisticated version of the table, by which they mean that it embodies the increasing length of periods with atomic number. Mendeleev himself produced a table which is essentially equivalent to the medium-long form as early as 1879. See van Spronsen, 1969, p. 138 for discussion. The modern form of the medium-long table dates from 1905 when it was introduced by A. Werner. (see van Spronsen, p. 152).

[7] Hettema and Kuipers define $\sim$ as a binary chemical similarity relationship, while e and e' are any two elements which stand in such a relationship. z serves to order the elements according to atomic weight.

[8] Mendeleev produced a total of about thirty different periodic tables in the course of his life.

[9] Mendeleev's earlier table of 1869 gives a sequence of 7, 7, 19, 19 . . . or 8, 8, 20, 20 . . . if the noble gases were to be included.

[10] The naive notion that a repetition of the elements should consistently occur after eight places is due to the British chemist Newlands, who is indeed generally credited with this discovery, as the authors themselves state in a different context.

[11] The order of filling is even more irregular than that suggested by this sequence. There exist about twenty exceptions to the simple aufbau scheme proposed by Bohr. This is one genuine sense in which the periodic table has not been reduced to quantum mechanics or atomic theory. Nevertheless, some recent group theoretical work has explained the sequence of 2, 8, 8, 18, 18 etc. in the order of filling of electron shells but not the anomalies mentioned above. (Kibler and Odabasi, 1973; Novaro, 1973; Kibler, 1989).

[12] Discussion of this point is resumed later in the present article.

[13] Quantum mechanics permitted successful calculations to be made on the energies of atoms other than hydrogenic ones.

[14] The authors quote a paper, by a philosopher, which seems to be the germ of this incorrect notion (Sundaram, 1985).

Even if we say there is an important shift from weight to number one would be hard put to find the crucial experiments to refute or corroborate the old and new 'programs'. (Sundaram, 1985, pp. 111–112)

In fact the experiments performed by Moseley serve precisely this function of falsifying the ordering principle based on atomic weight. Moreover, Sundaram is by no means an authority on the periodic table but one of a few philosophers to have touched on the subject in the literature in philosophy of science. Hettema and Kuipers fail to cite the main authorities on the periodic table such as van Spronsen.

[15] Other pair reversals involve cobalt ($Z = 27$) and nickel ($Z = 28$) as well as argon ($Z = 18$) and potassium ($Z = 19$). The correct symbol for atomic number, or capital Z, has been used here instead of z as the authors use throughout their article.

[16] The implicit introduction of atomic number should properly be attributed to Newlands who indeed went further than Mendeleev in giving the elements successive whole number labels based on their atomic weight ordering. Indeed he is the only one of the six acknowledged pioneers of the periodic system to have made this anticipation of the concept of atomic number.

[17] I am referring to such examples as the classification of spectroscopic states or the calculation of ground state energies, both of which properties show marked periodicities.

[18] With reference to the system of labeling groups from 1–18 as introduced by the International Union of Pure and Applied Chemistry (IUPAC).

[19] The outer-shell configurations of these three elements are, vanadium, $3d^34s^2$; niobium, $4d^45s^1$; tantalum, $5d^36s^2$.

[20] An even more marked example is shown by the three elements nickel, palladium and platinum each of which shows a different outer sub-shell configuration and yet all three elements are grouped together due to their marked close chemical analogies. The configurations are, Ni, $3d^84s^2$; Pd, $4d^{10}5s^1$; Pt, $5d^96s^1$.

[21] Indeed, strictly speaking, quantum mechanics forbids any talk of electrons in orbitals and hence electronic configurations (Scerri, 1991).

[22] The reduction is incomplete due to the failure to solve the many-electron Schrödinger equation, a point which will not be labored here. (Scerri, 1994a).

[23] The repeated identification by Hettema and Kuipers of z with the total number of electrons is incorrect. z should at all times be identified with the number of protons as is frequently emphasized in elementary courses in chemistry.

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THE PERIODIC TABLE: THE ULTIMATE PAPER TOOL IN CHEMISTRY

THE PERIODIC TABLE AS A PAPER TOOL

The term paper tool as well as similar ones like conceptual tools, tools of representation, and tool-box of science, have begun to creep into the literature, especially in the history of science. The first of these terms, paper tools, was coined by Ursula Klein (Klein, "Berzelian Formulas"). The other terms I mention, which evoke similar ideas have been used by the likes of Bruno Latour, Jed Buchwald and Nancy Cartwright in spite of their widely diverging philosophical orientations. In addition terms like "tools of representation" are sometimes used by scientists, in particular in the computational sciences. Since one theme of this volume is 'paper tools in chemistry and other experimental science' I will try to say a few words about how I interpret this phrase.

I take it that the first word is really a euphemism for *theoretical tools*. In other words we are dealing with tools which can be written on paper rather than with laboratory tools which can be used to affect chemical operations such as distillation or chemical analysis. Let us be clear that in the case of the periodic table this is not necessarily a *paper* tool. The periodic table shown in figure 1, for example, is made of plastic. It has several advantages over the more usual 2D versions in that it displays the inherent symmetry of the periodic law and can reveal more analogies between valences of elements than the usual medium-long form. For example, as well as aligning together the elements in group IIIA of the periodic table (boron, aluminum, gallium, indium, thallium) this representation also aligns these elements with scandium, yttrium, lanthanum, lutetium, actinium and lawrencium. All these elements also display a valency of 3 as showing well as some secondary chemical analogies with members of group IIIA.

Now it might be said that there is little difference between paper and plastic. Admittedly they both contain the elements C and H but that is where the similarity ends. There were other cases which were neither paper nor plastic but nonetheless a very useful periodic table that can even enlighten passers-by as to the delight of chemistry, such as the mural version to be found in St. Petersburg outside the Institute of Weights and Measures where Mendeleev worked for a number of years. Now if it is agreed that by paper tool we mean theoretical tool, then it is necessary to analyze the extent to which the periodic table is a theory or at least like a theory. This discussion has implications for the ongoing debate in history and philosophy of science regarding the relative importance which is attributed to successful predictions as opposed to successful accommodations by scientific theories or new discoveries (Brush, "Theory Change"; Lipton, "Prediction"; Scerri, "The Periodic Table"). The debate centers on whether successful predictions count more than

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accommodations as is commonly portrayed in scientific textbooks and even newspaper announcements.

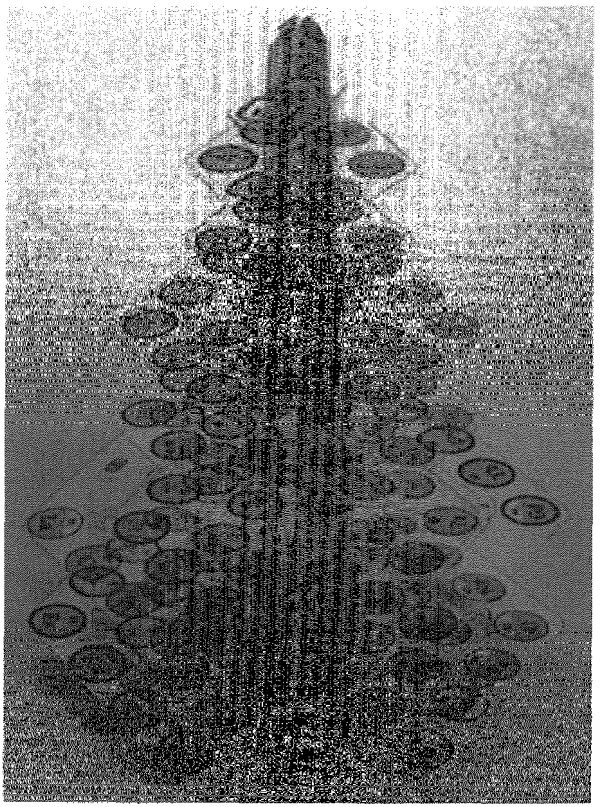


Figure 1. (photography kindly provided by the designer, Fernando Dufour)

Einstein's general theory of relativity is generally held to have been accepted because of making bold prediction of the bending of starlight which was subsequently confirmed by the Eddington expedition of 1919. Even the New York Times featured Eddington's observations as front-page news and proclaimed that Einstein's theory had been confirmed.

Nevertheless, careful historical work has shown that the issue is far from clear-cut. Steven Brush, from the University of Maryland, has been arguing rather persuasively that, in most of the theories he has examined, successful accommodation actually counted more than the dramatic, and sometimes, headline-grabbing predictions (Brush, "Theory Change"). As Brush has shown, Einstein's explanation of the previously known advance of the perihelion of mercury seems to

have contributed as much and perhaps more to the acceptance of his theory than the dramatic prediction of the bending of starlight referred to above.

THE ACCEPTANCE OF THE PERIODIC TABLE AND THE ROLE OF PREDICTIONS

The periodic table is also usually taken as a classic example in which successful prediction was responsible for the widespread acceptance of a scientific development. Interestingly, this is the only case in which Steven Brush is prepared to accept that, contrary to all the other cases he has examined, prediction was indeed the main factor responsible for the acceptance of Mendeleev's periodic.[1] The alleged importance of predictions is also stressed in nearly every chemistry textbook and even sophisticated historical treatments, where it is claimed that Mendeleev's system prevailed specifically because of his successful predictions (Scerri, Worrall, "Prediction").

But is it actually true? As I and others have argued, even in this case accommodation of already known facts may have counted at least as much as predictions. One of the complicating factors in trying to examine the case of the periodic system has been that theories in physics, such as general relativity and quantum mechanics do not have the same character as the periodic table, or the more fundamental 'periodic law'. Whereas in the case of physical theories the predictions follow almost inevitably from the theory, and the choice of boundary conditions, the same is not true of the periodic system. Indeed, Mendeleev's predictions on scandium, germanium and gallium do not even seem to follow precisely his own stated method.

The historical facts surrounding the classic predictions of a number of unknown elements, made by Mendeleev, show that he used a vast store of chemical intuition, rather than a straightforward algorithm as a physicist might. A clearer appreciation of the nature of the periodic law can be gained by considering how Mendeleev arrived at the specific details of his predictions on the elements gallium, germanium and scandium. Mendeleev himself gives a clear and unambiguous indication of this method in his textbook The Principles of Chemistry. He states that the method consists of simultaneous interpolation within groups or columns as well as within periods or rows of the periodic table. The procedure is carried out, very simply, by taking the average of the sum of the values of the four elements flanking the element in question. According to Mendeleev,

> If in a certain group there occur elements, R_1, R_2, R_3, and if in that series which contains one of the elements, for instance R_2, an element Q_2 precedes it and an element T_2 succeeds it, then the properties of R_2 are determined by the mean of the properties of R_1, R_3, Q_2 and T_2. (Mendeleev, *Principles*)

In the various editions of his textbook, and in the publications dealing specifically with his predictions, Mendeleev repeatedly gives this same example of calculating the atomic weight of the element selenium.[2] This value which was known at the time and could thus be used to test the reliability of this method.

However, if one attempts to apply this method to the prediction of atomic weights, atomic volumes, densities and other properties of gallium, germanium and scandium one arrives at values which differ significantly from Mendeleev's

published predictions. Rather amazingly, his published predictions turned out to be very accurate when compared with the properties of the subsequently discovered elements. This suggests great chemical intuition that allowed Mendeleev to make minor modifications to his stated method whenever it was necessary. Mendeleev appears to have deviated from his stated approach, but he somewhat mysteriously omitted to specify how and why he departed from the simple method of interpolation. I believe that this example illustrates the way in which the periodic law is not used in the same way that laws in physics are typically used to deduce consequences in a strict way. In physics once the algorithmic procedure has been established there is no such room for adjustment. At the hands of Mendeleev the periodic law seems to allow for small modifications to be made to what might otherwise have seemed like inevitable deductions.

Let me just repeat that what I am trying to understand here. It is the sense in which paper tools are 'paper' and the sense in which paper tools are 'tools' in chemistry. The periodic table is the prototypical paper tool in chemistry putting aside the provisos that I have already expressed about the words 'paper' and 'tool' in this context. If it is to be regarded as a theoretical tool then it is not of the same kind as a theoretical tool in the field of physics as I will try to explain. To maintain the analogy from craftsmanship, it appears as if this paper tool, at least, is more malleable than paper tools in physics.

PRE-HISTORY OF THE PERIODIC SYSTEM

Recently I have begun to write a book on the evolution and the meaning of the periodic system. I have given a good deal of thought to the pre-history of the periodic system, especially at the beginning of the nineteenth century with the work on triads of elements by Döbereiner and others. In looking into these matters I have been forced to examine the difficult history surrounding the use of atomic weights and equivalent weights prior to the Karlsruhe conference. My aim has been to look into not just triads, or vertical groups as they later became, but also the development of what might be called horizontal relationships among the elements. Unlike the case of triads these were the relationships between unlike elements and were more difficult to discern for several reasons.

Bernadette Bensaude-Vincent has written extensively on how Mendeleev's crucial stage in the evolution of his periodic system was the recognition of the need to consider relationships between dissimilar elements (Bensaude-Vincent, "Mendeleev's Periodic System"). In Mendeleev's case these were the alkali metals and the halogens. But, as she is no doubt aware, there were earlier attempts to make horizontal connections between the elements, although they were not as successful as those of Mendeleev. Such other attempts included those of the chemist Peter Kremers (Scerri, "Evolution").

FROM TRIADS TO HORIZONTAL RELATIONSHIPS IN THE EMERGENCE OF THE PERIODIC SYSTEM

The historical origins of the periodic system has received little attention from historians of science despite the obvious central importance of the periodic table in

the development of modern chemistry and physics, not to mention its continued use in present-day science. Although the names of Mendeleev, and to a lesser extent Lothar Meyer, are well known to chemists, as being those of the originators of the periodic system, the other co-discoverers of the system such as de Chancourtois, Odling, Newlands and Hinrichs are far less well known. Even less is usually appreciated about the earlier wave of discoveries which permitted these pioneers to formulate the various forms of the more mature periodic system. I am going to consider the scientists who paved the way for the discoverers of these mature forms of the periodic system. These early contributors recognized several groups of triads, that is various sets of three similar elements, which showed a definite relationship between their atomic weights. Some of these triads eventually formed parts of the vertical columns, or groups, which occur in the mature periodic system.

DÖBEREINER DISCOVERS TRIADS

First, it is worth mentioning that contrary to the accounts found in many chemistry textbooks Döbereiner's discovery of triads, whose middle member has approximately the mean atomic weight of the two flanking members, did not in fact concern elements but instead their compounds. In 1817 Döbereiner, a protegé of the German poet Johann Wolfgang Goethe, found that if the equivalent weights of oxides of calcium, strontium and barium were considered, the equivalent weight of strontium oxide was approximately the mean of those of calcium oxide and barium oxide.

$$SrO = (CaO + BaO) / 2 = 107 = (59 + 155) / 2$$

What is not often reported in modern accounts is that Döbereiner considered the possibility that the middle element might be a mixture of the other two elements in the triads he identified. He also considered that his observations might support the notion of transmutation between the three elements, another feature which, not surprisingly, tends to be written out of accounts of the evolution of the periodic system.

ATOMIC WEIGHTS AND EQUIVALENT WEIGHTS

It should be explained that at this stage in the history of chemistry the concept of atomic weight had only recently been introduced by John Dalton and nobody was quite sure about how it should be calculated. By contrast as early as the 1790s Richter had introduced the concept of equivalent weight that is the amount of one substance that reacts with a particular amount of another substance. Several chemists soon published lists of the equivalent weights of compounds, especially acids and bases which, as Richter had realized, reacted together in definite proportions in the course of neutralization reactions.

Equivalent weights thus had a clear experimental basis and did not rely on any form of theorizing about the existence of atoms or molecules. By contrast, Dalton's atomic weights, and those published by several of his contemporaries, were more theoretical in that they depended on assuming a particular formula for a compound,

something which could not be verified experimentally at this time. The case of water provides a very good example. Measurements of the amount of oxygen and hydrogen that react together led to the result that the equivalent weight of oxygen is eight relative to that of hydrogen. In other words, one gram of hydrogen always reacts with approximately eight grams of oxygen.

But unless the formula of water is known this tells us nothing about the relative weights of the atoms of hydrogen and oxygen. If the formula of water is assumed to be HO then the atomic weight of oxygen is eight just like its equivalent weight. This indeed is the conclusion arrived at by Dalton using his rule of maximum simplicity which stated that if two elements formed only one compound it would have a binary form such as HO in the case of water. Dalton assumed that if two elements, such as carbon and oxygen, for example, were to form two compounds these would have formulae of CO and CO_2, that is they would be binary and ternary respectively. He also allowed for the possibility of the formula being C_2O in the case of carbon and oxygen. Whereas Dalton's method gave an incorrect formula for water, in the light of subsequent knowledge, he was clearly more fortunate in the case of the oxides of carbon.

The question of finding the correct formulas for compounds was only conclusively resolved a good deal later when the concept of valency of any particular element was clarified by chemists like Frankland and Kekué. With this new knowledge the relationship between atomic weight and equivalent weight could be stated simply as,

$$\text{atomic weight} = \text{valency} \times \text{equivalent weight}$$

Oxygen was found to have a valency of 2 which means that whereas its equivalent weight is 8, as many early chemists had determined, its correct atomic weight is twice that number or 16.[3]

WHY WERE TRIADS DISCOVERED BEFORE HORIZONTAL RELATIONSHIPS?

Returning to triads, we can now begin to understand why it was that these vertical relationships among elements were discovered long before chemists began to notice what we would now call horizontal relationships, or periods, across the periodic table. The key point is that the elements within any one triad are now known to show the same valency. This means that whatever error may have arisen in using equivalent weights, instead of atomic weights, would have been a consistent error in all three elements concerned. Any such error would not have prevented the value for the middle element from being approximately the mean of the two other elements in the triad.

However, when it came to comparing elements which are now known to lie in a horizontal series, the error introduced by the use of equivalent weights, together with incorrect valences, to calculate atomic weights caused serious problems. Suppose we use the equivalent weights given by Woolaston's table of values published in 1814 in which O = 10, C = 7.54 and N = 17.54. If we try to order the elements according to just their equivalent weights we obtain the ordering C, O, N

which is incorrect in the light of modern knowledge.[4] We could assume that the elements carbon, nitrogen and oxygen all show valences of one in their simplest compounds with hydrogen and try to calculate their atomic weights.[5] According to this assumption the respective atomic weights of these elements are exactly the same as the equivalent weight in each case. If the elements are ordered according to increasing values of atomic weight calculated in this way we again obtain the mistaken sequence of carbon, followed by oxygen, followed by nitrogen, whereas we now know that nitrogen is the middle member of this short horizontal row of elements. In addition, the irregular gap between the values for these elements does not give the slightest indication that these three elements occur in adjacent positions as recognized in the modern table.[6]

But this example, which is a historical reconstruction of the kinds of arguments used by chemists at the time, does not even begin to show the deep confusion which existed in the field of atomic and equivalent weights for more than the first half of the nineteenth century.[7] In fact before the correct relationship between atomic and equivalent weights had been discovered some chemists regularly referred to atomic weights as equivalents and vice versa. To make matters worse, even if the same terminology was used by any two given chemists there were still disagreements as to values since various standards were used by different workers.[8]

In addition, the methods for obtaining atomic weights were only applicable to gases. Initially it was not possible to estimate the atomic weights of liquids and solids and this made it difficult to recognize periodic relationships since on crossing a period one typically moves from solids to gases, very occasionally passing though liquids. Not surprisingly therefore groups of similar elements in the periodic table were discovered long before periods involving dissimilar elements or, in other words, vertical relationships were discovered before horizontal ones.

Of course there is a more immediate reason as to why groups were discovered long before periods. This is the simple fact that elements within groups share chemical properties, thus rendering their grouping intuitively obvious. Although this is quite true what is being addressed here is the separate issue of the recognition of numerical relationships between elements in groups. The existence of the periodic table depends not only on chemical properties but also on numerical aspects and on physical properties of the elements.

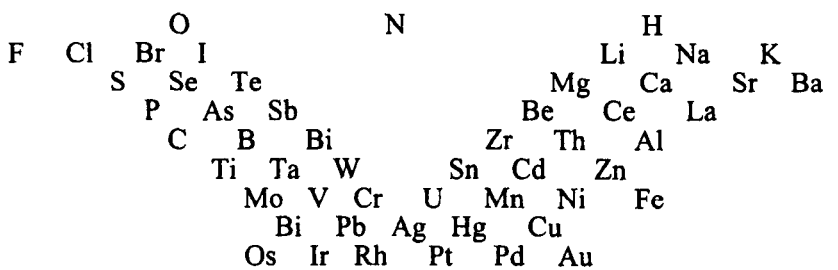
GMELIN'S REMARKABLE SYSTEM

In the course of my research for this paper I have stumbled across a much-neglected system of classification and I hope to show just how advanced this system was, especially considering the early date at which it was complied. The system in question was published in 1843, a full twenty-six years before the publication of Mendeleev's famous system of 1869 (Gmelin, *Handbuch*). I am referring to a little known system published by Leopold Gmelin, the same Gmelin who produced the rather voluminous *Handbuch der Chemie* and perhaps one of the most influential chemical writers of this time.[9] Although Döbereiner, as discussed earlier, is rightly regarded as the originator of the notion of triads, Gmelin also did much useful work in this area including his coining of the term 'triad'. For example, whereas Döbereiner had grouped magnesium together with the alkaline earths, he had failed

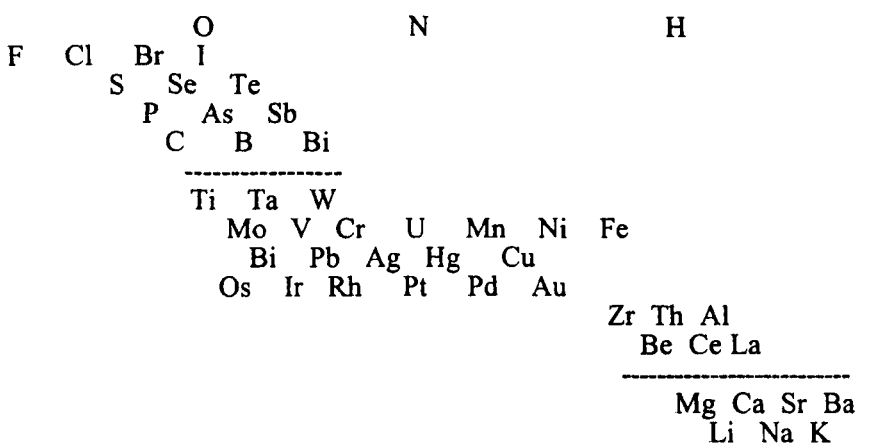
to find a triad relationship involving this and other alkaline earth elements whereas Gmelin noticed the following relationship,

$$(Mg + Ba) / 4 = Ca$$
$$(12 + 68.6) / 4 = 20.15 \quad (Ca = 20.5).$$

Let me now turn to what I think is really remarkable about Gmelin's system of 1843.[10] From the existence of four unconnected triads discovered by Döbereiner, Gmelin was able to make a huge leap forward in his version of 1843 in obtaining a system based on triads, or larger groups, consisting of as many as 55 elements. In addition the system as a whole was implicitly ordered according to increasing atomic weight although this has not been generally recognized before. With this work Gmelin succeeded in capturing the correct grouping of most of the then known main-group elements. This achievement has just not been appreciated by historians of chemistry or even historians of the periodic system.[11]



Suppose we take the arms of Gmelin's V-shape and make the right arm point down instead of upwards.



We can then rotate the entire table by ninety degrees and stack all the columns together

H	Li		C			F
	Na	Mg		P	S	Cl
	K	Ca		As	Se	Br
		Sr		Sb	Te	I
		Ba				

In this new table I include only the elements which Gmelin has grouped together and which correspond to modern day groupings among the main-group elements. In addition, I have omitted all the elements, between the dotted lines, which mostly consist of transition elements. Without being aware of what came to be called horizontal relationships, and without explicitly ordering the elements according to atomic weight, Gmelin appears to be anticipating both of these features in an extremely early periodic table. He has correctly placed the elements of what subsequently became group I next to those of group II. On the other side of the table he has correctly placed the first element of modern group IV, carbon, next to three of the elements in the modern group labeled as V. The next two adjacent grouping are even more remarkable in that Gmelin has correctly placed three elements of group VI next to three elements of group V and then has also correctly placed four of the five elements in modern group VII next to group VI.

What Gmelin's table achieves, granted this artistic license, is an essentially correct grouping of many of the representative, or main-group elements. Given the uncertainties, up to relatively recent times, regarding the inclusion of the transition metals and inner transition metals in periodic systems, the failure of Gmelin's system to arrange these particular elements correctly can hardly be taken as a reason for thinking any less of his system.[12]

The fact that Gmelin could produce such an arrangement of the remaining elements so early in the history of the evolution of the periodic system is rather remarkable. In the case of groups I, II, IV, V, VI and VII *all* elements are shown in the correct order of increasing atomic weight going left to right, except for boron and bismuth which are placed incorrectly in group 4. The only main-group misplacements appear to be nitrogen and oxygen but Gmelin clearly recognizes that oxygen belongs with S, Se and Te when he points out the following relationship,

$$O = 8, \quad S = 16, \quad Se = 40, \quad Te = 64, \quad Sb = 129 \quad = 1 : 2 : 5 : 8 : 16$$

Perhaps Gmelin's table cannot be properly called a periodic system since it does not depict the well known tendency of the elements to recur, that is to show periodicity, after certain regular intervals. Moreover, Gmelin's system does not *explicitly* arrange the elements in increasing order of atomic weight or even the previously used equivalent weights. But there is clearly an implicit use of atomic weight ordering since the placing of many of the triads, side by side, follows the correct order as found in subsequent more mature periodic systems and this does not appear to be a mere coincidence.[13]

In addition, Gmelin used his own rudimentary system of the elements, about 25 years before Mendeleev, to give an overall structure and direction to a chemical textbook.[14] Gmelin's is thus possibly the first chemistry textbook author to do so. Whereas it is Mendeleev who is usually credited with basing a textbook around the system of the elements, Gmelin gives the system immediately on the very first page, at the start of volume II of his series. The remainder of this volume is a detailed 500 or so page survey of the chemistry of 12 non-metallic elements.[15]

In addition, the order that Gmelin elects to follow in his presentation is dictated by his system of elements. He begins with oxygen and hydrogen, two of the three elements at the head of his table. The following chapters discuss the chemistry of carbon and boron that Gmelin has placed together in the same group. He then discusses the chemistry of phosphorus the only non-metal in group V of the modern table apart from nitrogen. This is followed by chapters on sulfur and selenium which are the non-metals in what became group VI of the table. Then comes a survey of the chemistry of all four of the then known non-metals in what became group VII of the modern periodic table.

Finally the volume closes with the chemistry of nitrogen, the remaining one of the three elements which Gmelin has placed at the head of his system of elements. Apart from the misplacement of boron, as mentioned earlier, Gmelin has given a systematic survey of most of the important non-metals in the order of groups IV, V, VI and VII, from the perspective of the mature periodic system, which only emerged with the work of Mendeleev in 1869.

This I submit suggests remarkable foresight and intuition, on the part of Gmelin, as does the way in which he uses his system to ground the presentation of the chemistry of these elements. The use of tables of elements as an important tool for giving structure to chemical textbooks, among other things, therefore appears to date from 1843 and not from the publication of the textbooks of Lothar Meyer and Mendeleev.

Gmelin's table is mentioned by van Spronsen, the author of the only scholarly history of the periodic system, but only rather dismissively.

> In 1843 Gmelin also tried to find a relationship between all elements. This however meant demoting the atomic weight. The elements O, N and H for which he apparently could find no homologues form the basis of his system.[16]

Thus van Spronsen fails to notice that Gmelin did in fact correctly classify at least one of these elements, namely oxygen, correctly with sulfur, selenium and tellurium. This is all the more surprising given that van Spronsen even mentions this fact himself on the same page although in a different context. Van Spronsen also criticizes Gmelin for not seeming to arrange the elements in order of increasing atomic weight. But as I have argued, Gmelin can not *but* have based his system on atomic weights, although perhaps implicitly and even a little erratically. It is difficult to see how, if at all, he can be said to have "demoted" atomic weight in producing his system, as van Spronsen claims. I propose that Gmelin's system should no longer be regarded as something of a footnote to Döbereiner's discovery of the existence of triads but as an important discovery of almost equal stature.

REPRESENTATION

The presentation of the periodic system seems to have held a tremendous fascination among experts and laypersons alike from the beginnings of the history of the system to the present day. What is the best way to represent the periodic system? Is there an optimum form of the periodic system?

Until quite recently I have argued in the literature that any particular mode of representation is secondary and to some extent almost irrelevant. For example, the author Edward Mazurs was able to collect together something like 700 different representations of the periodic system in his well known book to commemorate the hundredth anniversary of the discovery of the system (Mazurs, *Graphic Representation*). The fact that such a variety of successful systems can coexist, more or less peacefully, suggests that just how the periodic system is represented is not a crucial issue. No particular representation is refutable, as a theory might be, unless it commits internal inconsistencies.

While on this subject, it should be remembered that Mendeleev rendered a great service which has not really been heeded. Although he considered various possible representations he also emphasized that the important aspect of the periodic system was the existence of the periodic law. The fact that Mendeleev attached so much importance to the periodic law, qua law, has been especially stressed by Bernadette Bensaude-Vincent in her many articles on the periodic table (Bensaude-Vincent, "Mendeleev's Periodic System"). I believe that she is correct to do so and that the modern tendency to not even mention the periodic law, as such, is regrettable. The reason for this omission is presumably because of the prevalent notion that this law has now been explained away by the deeper laws of quantum mechanics (Scerri, "Explanation"). This is just not true and I will return to the issue later in this article.

However, to say that representation is secondary and that all that matters is the more abstract periodic law is to express a philosophical prejudice. This is an issue on which writers such as Pierre Duhem, Norman Campbell and more recently Mary Hesse have all written very eloquently (Duhem, *Physical Theory;* Campbell, *Science*; Hesse, *Models*). The question is whether the scientist should focus on models or, instead, on the more abstract mathematical relationships or laws. According to some of these authors British scientists, at least at the turn of the twentieth century, were more predisposed to building and thinking about models whereas continental scientists were more likely to dwell in just in the abstract laws and formalism. The development of quantum mechanics on the European continent would appear to be an example of the triumph of the abstract view of physical theories over the desire to regard the subatomic world realistically.[17]

But there is no denying the fact that sometimes it does help to concentrate on examining the properties of a model, be it visualiseable or mechanical. In a separate research effort I have been examining the reduction of the periodic system to quantum mechanics and trying to see the extent to which quantum mechanics explains the periodic system. It turns out that the explanation found in nearly all textbooks, even advanced treatments, are claiming too much on behalf of quantum mechanics. The false impression created is that the form of the periodic law can be deduced from quantum mechanics without recourse to any experimental data. In fact the explanation is semi-empirical in that it does depend rather crucially on

experimentally obtained information. Occasionally one sees a more honest version given in a book such as the following in Max Born's classic treatise on Atomic Physics.

In a section appropriately entitled *The Periodic Table* Born begins by giving the customary explanation for the occupation of orbitals by the first eighteen electrons according to the relationship between the four quantum numbers and the restrictions of the Pauli principle. He then writes,

> Then however a deviation occurs from the apparently natural order of succession in which the electrons settle. This order is always determined by the energy released when a new electron settles (i.e. is bound). The energy relations, however, are not always such that one shell must be completed before an electron settles in the next shell. On the contrary it may happen that an electron in an s orbit of a higher shell is, from the energy point of view, more firmly bound than in a d- or f-orbit of the lower still incomplete shell. This case occurs in the further development of the M shell; the ten 3d-terms for the ten electrons still wanting are, *as experiment shows*, higher as regards energy than the 4s terms which correspond to binding of the electrons in the N shell. The next two electrons to be added (K, Ca) settle therefore in the N shell. (Born, *Atomic Physics*, 183–184; italics added for emphasis)[18]

Most textbook accounts unfortunately omit any mention of "as experiments show". The point is that the usual textbook explanation only works deductively to predict the number of electrons in each shell and this is of course a great triumph of the theory. But there is more to explaining the periodic table than merely deducing the number of electrons which any of the shells can contain.

The electron shells do not fill sequentially. The order of filling is obtained experimentally as Max Born concedes. Although some aspects of the observed ordering can be explained, after the facts, these explanations begin to take on the appearance of Ptolemaic epicycles of increasing complexity (Bills, "Energies"; Nelson, "Relative Energies"; Pilar, "4s"; Scerri, "Orbital Approximation"; Vanquickenborne et al., "Aufbau Principle").

What is required is a more fundamental explanation that allows one to deduce the length of the periods from first principles and not just the number of electrons that any shell can contain. Maybe this will require a deeper theory than present quantum mechanics, just like the removal of Ptolemaic epicycles had to await the discovery of the heliocentric model of the solar system. I don't know what exactly is required. What I do know is that if we have every right to go on asking such questions and requiring that the theory predict what has up to now been explained semi-empirically (Emerson, "Explanation"; Scerri, "Explanation").

Let me be quite clear. What I think is needed is a theoretical explanation of the particular pattern of period lengths such as 2, 8, 8, 18, 18, 32 etc. and not merely the fact that any period can have a length of 2, 8, 18, or 32 etc. This is why I have recommended the use of the pyramidal representation of the periodic table which highlights this feature rather than burying it in the details and the footnotes as does the usually seen medium-long and even the long form (Scerri, "Electron", "Evolution").[19]

So I would like to see this representation used as a challenge to theoretical chemists and physicists and to serve as a reminder of a feature that is not yet fully explained from quantum mechanics. Rather than claiming that the periodic table does not reduce to quantum mechanics I am really trying to encourage physicists to dig deeper and give an even more reductionist explanation of the periodic system.

When all is said and done, I suppose I am still maintaining that the model or the representation of the periodic table is indeed secondary. From a theoretical point of view it is a means to an end since the goal is a theoretical deduction of the observed facts. To the chemist of course representation must offer something useful which suits his or her particular purpose. So the demand for representation, not surprisingly is context dependent. It depends on what purpose one is putting the periodic system to.

One upshot of these ideas might be that a paper tool may also be something which leads to a deeper theory. It is of course well known that the periodic table has led to several advances in theoretical physics. J. J. Thomson's electron rings were developed in what was the first attempt to give a microscopic explanation for the periodic system. Thomson even stated that the explanation of the periodic table was one of the outstanding problems which theoretical physics had to meet. Niels Bohr's initial inspiration for applying the quantum of action to the atom also came in attempts to understand the periodic system theoretically, in examining the details of Thomson electron-ring explanation of the periodic system. Wolfgang Pauli's enormously far-reaching Exclusion Principle may be given as another case where attempts to explain aspects of the periodic system. In this case the number of electrons which any shell can hold, led to an important discovery in theoretical physics whose application went well beyond the confines of chemical periodicity.

CONCLUSION

In spite of the long-standing rhetoric in philosophy of science about the need to give more attention to models rather than theories, or linguistic aspects in general, the question of paper tools in science remains neglected. In chemistry in particular this seems inexcusable given the obvious importance of formulas and molecular representations of all kinds. In addition, the central icon of chemistry, the periodic table, is a vitally important paper tool that has not been reduced by appeal to the putative underlying theory. Perhaps it would be better to put more attention on paper tools, as many contributions to this volume have started to do, instead of attending exclusively to theories or even mathematical models. Even if one is to follow the current vogue of concentrating on models it is important to recognize that paper tools are an important class of models with interesting new aspects which are not subsumed by the study of models in general.

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NOTES

[1] Actually Brush has equivocated a good deal. Whereas he began by stating that predictions counted more than accommodations in his paper (Brush, "Theory Change"), more recently he has given a rather confusing conclusion. In one place he says that predictions counted more whereas elsewhere in the same paper he says that predictions are only the third most important factor behind accommodation and correction of weights of known elements.

[2] Mendeleev might just have used the values for 8 flanking elements or in the case where two proximate elements were missing he could have used diagonally placed flanking elements.

However no calculations based on eight elements or diagonal triads appear to reproduce exactly the predictions published by Mendeleev.

[3] I have given a simplified account throughout this section. The reader interested in a more in-depth treatment should consult the publications of Alan Rocke (*Chemical Atomism*, "Atoms"). I would like to thank him for his help over this issue. He probably knows more about the question than anyone else and was kind enough to send me some unpublished material from a book which he was currently still working on.

[4] The correct order is C, N, O.

[5] In fact the formulas are CH_4, NH_3 and OH_2 (or H_2O) respectively instead of CH, NH and OH.

[6] The correct sequence of elements is more critical in moving across a period since this concerns consecutive elements with values closer to each other than members of a vertical triad or elements.

[7] Interestingly the use of some sets of atomic weights known at the time, instead of equivalent weights, would have led to the correct ordering of these three elements by this type of calculation. See van Spronsen, *Periodic System*, 46–47.

[8] Details from Ihde regarding standards for atomic weights. See my notes Green Book.

[9] Rather than being literally a "hand" book this work amounted to massive 18 volumes.

[10] Of course what I say may strike some of you historians as Whiggism but there is no doubt for example that historians of chemistry regularly ask who was the first person to base a system of the elements on atomic weights or equivalent weights. Is this Whiggism just because it turned out that the ordering of the elements by some numerical criterion was an important if not crucial ingredient? If you accept that there is some worth in this question you may also accept that there is some value in asking who was the first person to establish a system for all the known elements, however dimly, among the elements.

[11] Surprisingly the excellent book on the early history of the periodic system written by Venable fails to even mention Gmelin's system.

[12] Gmelin can hardly be held accountable for the misplacement of transition metals since such problems were common even in later, more mature, periodic systems.

[13] If one examines the later system of Gladstone which is almost exclusively based on Gmelin's system under discussion, this reveals that Gmelin did in fact order most elements according to trends in their atomic weights. Indeed Gmelin was very interested in values of atomic weights and in 1827 produced an early list which included atomic weights for as many as 45 elements.

[14] Whether to present chemistry inductively or deductively is of course ultimately a matter for each author's philosophical taste. It is by no means clear that Mendeleev's apparent decision to proceed inductively is the only correct option.

[15] Mendeleev's only displayed his own periodic sysytem in volume II of *The Principles of Chemistry*. It is also common knowledge that when he began writing his two volume textbook he had not yet discovered the periodic system. This only dawned on him after he had completed volume I which remained largely unrevised in subsequent editions.

[16] (van Spronsen, *Periodic System*, 70).

[17] The one case that contradicts this notion is perhaps the most abstract work of all, in the pioneering stages of the development of quantum mechanics, by the British physicist Paul Dirac. Nevertheless Dirac was of Swiss heritage and grew up speaking French.

[18] See Born, *Atomic Physics*.

[19] In addition, the pyramidal forms also have a chemical advantage in highlighting so called secondary chemical relationships as I mentioned at the start of the article and illustrated in fig 1.

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4

Realism, Reduction, and the "Intermediate Position"

ERIC R. SCERRI

The editors of this volume have asked me to write something about reduction because I have been focusing on this issue in my research for some time.[1] Rather than rehashing any previously published ideas, I want to consider a new aspect of this question—or at least one that is new to me.

I will draw liberally on the work of my thesis grandfather, the chemist, Fritz Paneth. I use the term somewhat unusually, because Paneth was not the person who advised my own advisor Heinz Post but was, in fact, his natural father,[2] from whom Heinz presumably developed an interest in the philosophical aspects of science.[3] I will touch on such areas as realism, including naive realism, the nature of the periodic system, metaphysical aspects of chemistry, and, as suggested by the editors, the reduction of chemistry.

Realism, Atomic Orbitals, and Chemical Education

Of course, nobody likes to be referred to as a naive anything, and not surprisingly, some chemists are quick to react if it is suggested that they tend to adopt a naively realistic attitude in their work.[4] Nevertheless, I think it is true that chemists are often realists, naive or otherwise, and this may not be such a bad thing, as I will try to explain. The question hinges on the extent to which such realistic views are maintained and in what context they may or may not be appropriate.

Broadly speaking, chemists are frequently accused of unwarranted realism by physicists for taking chemical models too literally. Whereas no chemist nowadays believes that tiny springs connect the atoms in a molecule, such denials of models are less prevalent when it comes to hybridization, electronic configurations, and atomic orbitals. Chemistry professors may well begin by declaring that these are approximate concepts, but they frequently fail to emphasize that, from the point of view of physics, they are strictly incorrect or, philosophically speaking, are nonreferring terms. But I contend that to describe something as an approximation does not carry quite the same ontological force of stating it to be nonreferential, and, according to current physics,

I repeat, only the latter is correct. Another way of putting this situation is to say that, in the case of many-electron atoms, atomic orbitals cannot be reduced to quantum mechanics.[5] However, such orbitals are regularly discussed and pictured in glorious color diagrams by chemists as though they were real and concrete entities. In fact, orbitals have become the lingua franca of modern chemistry at all levels from introductory to advanced research.

It is interesting to examine why such an apparently mistaken view has developed among chemists. To put the question starkly: How is it that if many-electron orbitals cannot be reduced to quantum mechanics, nevertheless, many chemistry textbooks begin with a thorough treatment of orbitals, quantum mechanics, atomic structure, electronic configurations, and the like? Are chemical educators merely oblivious of the work of physicists and philosophers who maintain that this reduction is not tenable? Is it because the reduction of chemistry is one case in which one can ignore these pronouncements, perhaps because chemistry lies so close to physics, and that there exists an intuitive belief that chemistry is, in principle, reducible to physics? Or is it perhaps due to some as yet unarticulated justification which implies that chemical educators know what is best for teaching chemistry regardless of philosophical debates on reduction and what physicists might say?[6]

A popular response has been to claim that chemical educators are wrong to base the presentation of chemistry so closely on quantum mechanics in view of the failure of the reduction of chemistry, including the failure to reduce many-electron orbitals. This response has been urged by several authors, including myself in the past (Scerri, 1991a), but I have recently suggested a revised view (Scerri, 2000). The view that I am starting to advocate is that chemical educators should continue to use concepts like orbitals and configurations, but only while recognizing and emphasizing that these concepts are not directly connected with orbitals as understood in modern quantum mechanics but are, in fact, a relic of the view of orbits in the so-called old quantum theory. One might even consider calling them "chemists' orbitals." Such a view is consistent with the notion of chemistry as an autonomous science. The concepts of chemistry cannot be reduced to quantum mechanics but at the same time we should not conclude that chemistry and physics are disunified—as some authors have implied—about all the special sciences (Galison & Stump, 1996). The chemist may, and perhaps should continue to be a realist about orbitals, but hopefully in not too naive a fashion.[7]

Better still, the view I am proposing now is an intermediate position between the realism of believing in the real and concrete existence of many-electron orbitals and the reductive view from quantum mechanics that banishes all talk of orbitals. I suggest that chemical education can benefit from a form of realism, which is tempered by an understanding of the viewpoint of the reducing science but which does not adopt every conclusion from that science.

Has the Modern Periodic System Been Reduced to Quantum Mechanics?

Another way to ask whether chemistry has been reduced to physics is to consider one of its central laws, the periodic law, to see whether it has been "explained away" by

quantum mechanics. As a matter of fact, the periodic law has not been reduced in this way. What the periodic law embodies is the approximate repetition of the elements after certain regular but varying intervals in the atomic number sequence of the elements have been traversed. More specifically, the lengths of the periods are, respectively, 2, 8, 8, 18, 18, 32, etc. The frequently made claim is that quantum mechanics has reduced the periodic system through the use of the Pauli Exclusion Principle and by assigning four quantum numbers to each electron. This approach serves to explain the above sequence in a semiempirical manner, a fact that textbook presentations do a good job of concealing (Scerri, 1998b).

Such an explanation is semiempirical because the order of electron subshell filling must be assumed by reference to experimental data. As the noted theoretician Löwdin (1969) has pointed out, the order of filling has yet to be derived from quantum mechanics. This feature is related to the well-known failure of quantum mechanics—or of any other form of mechanics for that matter—to provide exact solutions to the many-body problem, thus rendering the quantum mechanical reduction of the periodic system approximate rather than exact. Although the failure of quantum mechanics to solve the many-body problem is readily acknowledged, the sleight of hand that admits experimental information into the alleged explanation of the periodic system is seldom even suspected (Scerri, 1997b). In any case, it should still be possible to explain the order of shell filling without solving the many-body problem. It has just not yet been done.

The way the periodic system is displayed in contemporary chemistry also contributes to the false impression that quantum mechanics explains the system deductively. The almost universally displayed form of the table nowadays is the so-called medium–long form in which the rare earth elements are shown as a footnote to the main body of the table (figure 4.1). The remainder of the table is divided into the s, d, and p blocks, respectively, reading from left to right. These labels, which have a spectroscopic origin (sharp and diffuse, from the type of observed lines), refer to the type of orbital that is supposed to contain the differentiating electron in each atom. A casual glance at this table reveals a rather obvious lack of symmetry.[8] This type of periodic table somewhat masks the fact that the length of the periods cannot be deduced from quantum mechanics and makes the s,p,d, and f classification,[9] referring to the filling of atomic orbitals, appear to be fundamental. Given the key role that symmetry principles have played in modern physics and chemistry, it would seem desirable to display the inherent symmetry of the periodic system rather than hiding this feature. However, the rather asymmetrical medium–long-form table, which I claim gives an exaggerated impression of the role of quantum mechanics in chemistry, is now well entrenched.[10]

An alternative form of the periodic table (figure 4.2) consists in the pyramidal form, which has been proposed by many authors[11] throughout the history of the periodic system and, indeed, was favored by Niels Bohr when he gave one of its first approximate quantum theoretical explanations.[12] As I have suggested before, the as-yet unexplained symmetrical aspect of the lengths of periods would be more likely to be addressed if this feature were displayed in the modern periodic table (Scerri, 1998b). In making this suggestion I regard the periodic law to be first and foremost a *chemical* law concerning the point at which the elements appear to recur approximately—or, in other words, that the essential content of the law lies in the sequence of numbers denoting the closing of the periods (2, 8, 8, 18, 18, 32, etc.) This sequence differs from

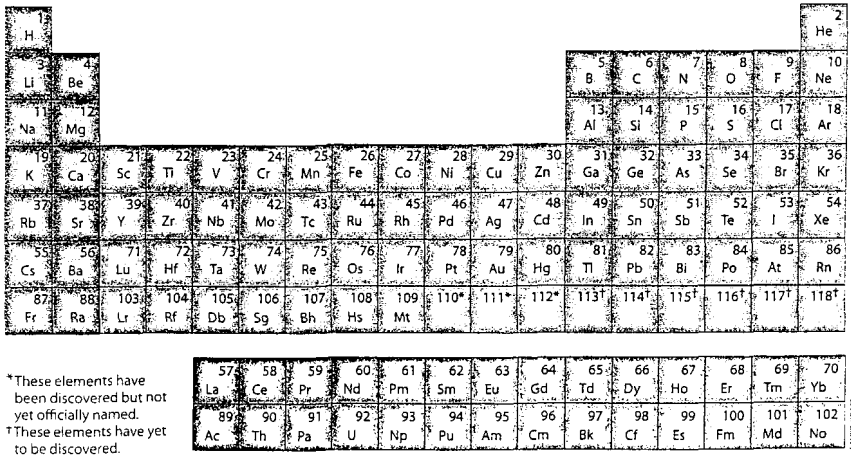

Figure 4.1 Popular Periodic Table—known as the medium-long form—this table can be found in nearly every chemistry classroom and laboratory around the world. This version has the advantage of clearly displaying groups of elements that have similar chemical properties in vertical columns, but it is not particularly symmetrical.

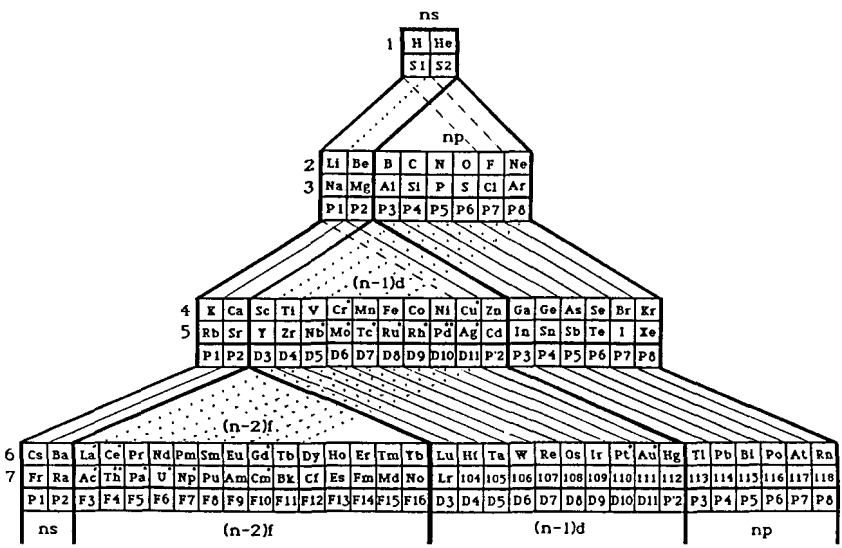

Figure 4.2 Pyramidal periodic table.

the sequence denoting the closing of the shells (2, 8, 18, 32). Only the latter has been deduced strictly by means of the Pauli Exclusion Principle and the relationships that hold between the four quantum numbers (Scerri, 1997b, 1998b).[13]

In insisting on this point I believe that I am adopting a more philosophical approach to the periodic system than is usually encountered in chemistry and physics. I am suggesting that the essence of the periodic law may still be hidden from complete view and that the failure to strictly predict the points at which the periods close is one symptom of our present lack of a full understanding of the law. Perhaps it is even the case that the periodic system which is concerned with the abstract elements will always remain somewhat hidden from full view.[14]

Paneth on Naive Realism and Transcendental Elements

Let me now turn to what Paneth, an inorganic chemist and one of the founders of radiochemistry, had to say about naive realism in chemistry:

> Chemistry, like every natural science, started from the naive-realistic world-view, and gradually found itself compelled to apply corrections to this. It is, however, characteristic of chemistry that it has not advanced as far in the application of these corrections as some other sciences; indeed it is of the essence of its fundamental concepts that they have retained quite an appreciable "naive realistic" residue. . . . Nobody objects, in fact, to speaking of the salty taste of sodium chloride, or the unpleasant smell of hydrogen sulphide. Here we find ourselves, as is surely unnecessary to elaborate, still standing with both feet on the ground of naive realism without, it should be emphasized, being aware that this lack of philosophic clarity entails any disadvantage. Indeed even in the case of that "property of substances" which can be reduced to quantitative determination most easily—color—we usually refrain, for the purpose of chemical characterization, from so reducing it: cinnabar "is" red, gold "is" lustrous. While the introduction of various constants would make a more exact numerical statement possible in such cases, this would be too cumbersome. (Paneth, 1962, p. 5)

And yet Paneth goes to great pains to point out that naive realism is not always the appropriate attitude to adopt in chemistry:

> Taking the philosophically primitive standpoint chemists have usually managed very well in the whole vast range of the subjects of analysis and synthesis. For this reason they have remained unaware that, after all, somewhat deeper epistemological consideration is necessary for the complete understanding of the reactions they have carried out and the theorems they have put forward. (Paneth, 1962, p. 9).

The main case in which Paneth believes we need this deeper outlook concerns the nature of the term *element* and what he calls the law of conservation of elements. Paneth wonders how the elements manage to survive intact in any compound they might find themselves in. To answer this question, he refers to a long-standing notion in chemical philosophy—namely, a view that the elements are the bearers of properties and, being so, are completely unobservable. According to this view, the elements are thought to inhabit what Paneth terms a "transcendental world."[15] Paneth also suggests that this view, which began with the Aristotelian notion of the elements and was upheld by the alchemists, was not altogether banished in the course of Lavoisier's chemical revolution,

as most historians of chemistry would have us believe.[16] He analyzes the philosophical writings of Mendeleev to show that even the discoverer of the periodic system held a similar philosophical view on the nature of the elements.[17]

Paneth considers it useful to distinguish two senses in which the expression "chemical element" is used. He refers to these two senses as *basic substance* and *simple substance:*

> I suggested that we should use the term "basic substance" whenever we want to designate that which is indestructible in compounds . . . and that we should speak of a "simple substance" when referring to the form in which such a basic substance, not combined with any other, is presented to our senses. (Paneth, 1965, p. 65).

In the case of element as a basic substance, Paneth claims:

> We cannot ascribe any particular qualities to an element as a basic substance, since it contributes to the production of an infinite variety of qualities which it exhibits both when alone and in combination with other basic substances . . . (Paneth, 1965, p. 65)

> With the concept of simple substance we may remain within the realm of naive realism. When we are concerned with the basic substance, however, we cannot disregard its connection with the transcendental world without getting involved in contradictions. (Paneth, 1965, p. 66)

I believe that Paneth makes an interesting case for this philosophical position that he shares with Mendeleev, and I would like to speculate further along the same line of thought because I think it can answer a specific question in the history of chemistry. As is well known, two men, Mendeleev and Lothar Meyer, independently arrived at the mature form of the periodic system in the late 1860s. Recently, there has been a lot of debate in the history and philosophy of science literature on the question of whether the periodic system was accepted because of its dramatic predictions or because of its successful accommodation of chemical facts (Maher, 1988; Lipton, 1990; Scerri, 1996; Brush, 1996). I happen to believe that accommodation may have counted as much as prediction but will not pursue this question here.[18]

One aspect beyond dispute is that Mendeleev made far more successful predictions than any of the codiscoverers of the periodic system. For example, he successfully predicted new elements, corrected the atomic weights of a number of known elements, and correctly reversed the positions of the elements tellurium and iodine. Why was it Mendeleev and not Lothar Meyer or others who was able to make such notable predictions? Is it simply that the others lacked the courage to do so, as many historians of science state?[19] I suggest that Mendeleev had the advantage of being blessed with a deeply philosophical approach to chemistry, which allowed him to arrive at insights that his less philosophically minded contemporaries could not have reached.

Like Paneth, he believed that the elements are essentially unobservable. He also believed that the periodic system should classify the unobservable basic substances in preference to simple substances. For example, the elements in the halogen group (fluorine, chlorine, bromine, and iodine) are rather different if we focus on the isolable simple substances that are gaseous, liquid, and solid, respectively. The similarity between the members of the group are more noticeable when it comes to the compounds of each one with sodium, for example, which are all crystalline white powders. The point is that in these compounds—fluorine, chlorine, bromine, and iodine—are not

present as the simple substance but present in a latent form. This has been described as a metaphysical view of the elements but should perhaps to be termed, as Paneth suggests, a "transcendental view."[20] In other instances, such as his correction of atomic weights, this transcendental view of the elements allowed Mendeleev to maintain the validity of the periodic law even in instances where experimental evidence seemed to point against it. Had he been more of a positivist, he might easily have lost sight of the importance of the law and might have harbored doubts about some of his predictions.

Some support for my speculation comes from the following opening statement by Klutgen writing in the journal *Philosophy of Science* in 1958:

> Dimtri Mendeleev while not creatively a philosopher of science, nor a student of systematic philosophy, was eminently a philosophical scientist. Concern about the nature and foundations of his science is evident throughout the text and footnotes of *Principles of Chemistry*. One has to presume that his conclusions provided him some direction for the study of his great generalizations in chemistry, especially for the greatest fruit of his efforts, the periodic System of the Elements. At least it is apparent that somehow he acquired greater confidence in the feasibility of systematizing extant chemical knowledge than almost any of his contemporaries. (Kultgen, 1958, pp. 177–183)

It would seem necessary at this point to say something about the earlier element schemes, especially the nineteenth-century scheme, and how it was that elements were regarded as transcendental and at the same time were characterized by such properties as their atomic weight. This task will be attempted in the following section.

Early Element Schemes, Especially the Nineteenth-Century Version

For Aristotle, the elements themselves are unobservable and transcendental (in Paneth's terminology), although they give rise to all the variety we see before us. The four elements (fire, earth, water, and air) are regarded as property bearers and are responsible for the properties of substance, although they are themselves unobservable. The elements are immaterial qualities impressed on an otherwise undifferentiated primordial matter and are present in all substances. Furthermore, the properties of substances are governed by the proportion of the four elements present within them.

This view was first seriously challenged by Lavoisier during the course of the chemical revolution. Lavoisier's new chemistry drew on the Aristotelian tradition but also included some new aspects. The new chemistry introduced the concepts of *simple substance* and *material ingredient* of substances. A simple substance is one that cannot be decomposed by any known means. The inclusion of the word *known* is very important because the scheme proposes that simple substances are to be regarded as such only provisionally and that they may lose their status following future refinements in analytical techniques. It is, one might say, a restrained view of scientific progress that recognizes the limitations of chemical analysis. As a result of Lavoisier's work, it thus became a relatively simple experimental question to determine which substances were simple and which were not. A major departure from Aristotle's scheme was that not all substances had to contain every one of these simple substances. There was no longer thought to being one undifferentiated primordial matter but that instead there

were a number of elementary constituents or simple substances were now possessed of observable properties such as weight.

A consequence of Lavoisier's scheme is that abstract elements do not necessarily correspond to particular known simple substances. It is possible that what is regarded as a simple substance at a particular stage in history may turn out to be decomposable as a result of subsequent advances in chemical analysis. Stated another way, to be certain of the correspondence between a simple substance and an abstract element one would need to have perfect confidence in one's analytical techniques. To his credit, Lavoisier only provisionally identified simple substances that had been isolated with abstract elements.[21]

And, yet, the transcendental aspect of elements was not completely forgotten and continued to serve an explanatory function in nineteenth-century chemistry but not necessarily a microscopic explanation. A chemist could be skeptical of atomistic explanations, as many were in the nineteenth-century, and yet could readily accept a transcendental explanation, for example, for the persistence of the elements in their various compounds. As was alluded to earlier, one of the benefits of regarding the elements as having a transcendental existence is that it provides a way out of the apparent paradox concerning the nature of elements when combined in compounds. Suppose that sodium and chlorine are combined to form sodium chloride (common salt). In what sense is the poisonous metal sodium present in a sample of white crystalline common salt? Similarly, one may ask how it is that the element chlorine, a green and poisonous gas, continues to exist in common salt. Clearly, the elements themselves, in the modern sense of the word, do not appear to survive, or else they would be detectable and one would have a mixture of sodium and chlorine able to show the properties of both these elements. The response available from the nineteenth-century element scheme is that simple substances do not survive in the compound but abstract elements do.[22]

According to the nineteenth-century scheme, these abstract elements are believed to be permanent and responsible for the observable properties of simple bodies and compounds.[23] However, in a major departure from the Aristotelian view, the abstract elements are also regarded as being material ingredients of simple bodies and compounds. The concept of material ingredient thus serves to link the transcendental world of abstract elements and the observable, material realm of simple substances. For example, the stoichiometric relationships observed in chemical changes are explained in terms of amounts of abstract elements present in the reacting substances through this concept of material ingredient.

Thus, we have three important concepts in the nineteenth-century scheme initiated by Lavoisier considerably earlier. The abstract element is a property bearer and owes its heritage to the Aristotelian element scheme. In addition to being a property bearer, the abstract element is an indestructible material ingredient of substances,[24] and as we saw in the preceding discussion, there is a fundamental distinction between abstract element and simple substance. Abstract elements are unobservable, whereas simple substances such as sodium, chlorine, and oxygen are observed. It should be noted that in contemporary chemistry we only seem to retain the latter notion in that the term *element* now means what to a nineteenth-century chemist would have been called a *simple substance*.[25]

The culmination of the nineteenth-century element scheme occurred with the discovery of the periodic system and with the work of Mendeleev, who more than any

other of the discoverers was concerned with the philosophical status of the elements (Mendelejeff, 1871). As stated earlier, Mendeleev was keenly aware of the abstract element/simple substance distinction, and he also realized that abstract elements, or basic substances, were to be regarded as more fundamental than simple substances. The explanation of why "elements" persist in their compounds was to be found in abstract elements and not simple substances, and, as a consequence, if the periodic system was to be of fundamental importance, it would primarily have to classify the abstract elements. Thus, the predictions that Mendeleev made were conceived of with abstract elements in mind. If the available observational data on simple substances pointed in a certain direction, these features could be partly overlooked in the belief that the properties of the more fundamental abstract elements might be other than had been observed up to that point. Of course, contact with observational data would still have to be the test of Mendeleev's predictions, but because the abstract elements were bearers of observable properties or, more specifically, a material ingredient in the form of the atomic weights of the elements,[26] these ideas could be tested empirically. As I have already speculated, it may be that Mendeleev's adherence to a more fundamental realm provided him with greater latitude in making predictions, and was the one of the key features that allowed him to make predictions that were far more successful than those of his competitors.

I will give just one example to illustrate Mendeleev's deep insight.[27] The metal beryllium provided one of the most severe tests for Mendeleev's system. The question was whether to place beryllium in group II above magnesium or in group III above aluminum. Its measured specific heat of 0.4079 indicated an atomic weight of 14, which would place beryllium in the same group as the tri-valent aluminum (Nilson & Petterson, 1878). Furthermore, beryllium oxide is weakly basic, the lattice structure of the metal is unlike that of magnesium, and beryllium chloride is volatile just like aluminum chloride. Taking these facts together, the association of beryllium with aluminum appears to be compelling.

Despite all this evidence, Mendeleev supported the view that beryllium is di-valent using chemical arguments, as well as considerations, based on the periodic system. He pointed out that beryllium sulfate presents a greater similarity to magnesium sulfate, than to aluminum sulfate and that whereas the analogues of aluminum form alums, beryllium fails to do so. He argued that if the atomic weight of beryllium were 14, it would not find a place in the periodic system. Mendeleev noted that such an atomic weight would place beryllium near nitrogen, where it should show distinctly acidic properties, as well as having higher oxides of the type Be_2O_5 and BeO_3, which is not the case. Instead, Mendeleev argued, the atomic weight of beryllium might be approximately 9, which would place it between lithium (7) and boron (11) in the periodic table.

In 1885 the issue was finally conclusively settled in favor of Mendeleev by measurements of the specific heat of beryllium at elevated temperatures. These experiments pointed to an atomic weight of 9.0, in reasonable agreement with Dulong and Petit's law and supported the di-valency of the element (Humpidge, 1885). Above all else, Mendeleev persisted in the belief that beryllium lies in group II because of his faith in the validity of the periodic law, which he believed was essentially a feature of the transcendental elements. All else was rationalized around this central tenet.[28]

By contrast, although some predictions were made by Lothar Meyer, Newlands, Odling, and other pioneers of the periodic system, these pale into insignificance when

compared with the predictions by Mendeleev.[29] At the risk of appearing to be proselytizing, I think that this provides a good example of why we need a philosophy of chemistry at present as much as it was needed in Mendeleev's days. (It is to be hoped that this book[30] will help revive the philosophical study of chemistry, or the "central science" as it is often called, and that thinking philosophically about chemistry will reap rewards in real chemistry research and not just serve to build up a new subdiscipline in philosophy.)

Whereas Mendeleev was clearly ahead of his competitors when it came to the prediction of elements, he does not seem to have fared so well with regard to his views on the reduction of chemistry. More specifically, his denial of the reduction of chemistry has generally been held to have been mistaken, especially in view of the subsequent discoveries of radioactivity and the structure of the atom. That such a conclusion has been reached by historians of chemistry is not at all surprising, especially given some of Mendeleev's own pronouncements on the subject:

> The periodic law . . . has been evolved independently of any conception as to the nature of the elements; it does not in the least originate in the idea of a unique matter; it has no historical connection with that relic of the torments of classical thought. (Mendeleev, 1905, vol. 2, p. 497)

> The more I have thought about the nature of the chemical elements, the more decidedly I have turned away from the classical notion of a primary matter, and from the hope of attaining the desired end by a study of electrical and optical phenomena. (Mendeleev, 1905, vol. 1, p. XIV)

> By many methods founded both on experiment and theory, has it been tried to prove the compound nature of the elements. All labour in this direction has as yet been in vain, and the assurance that elementary matter is not so homogeneous (single) as the mind would desire in its first transport of rapid generalization is strengthened from year to year. (Mendeleev, 1905, vol. 1, p. 20)

> The periodic law affords no more indication of the unity of matter or of the compound character of our elements than the law of Avagadro. (Mendeleev, 1905, vol. 2, p. 498)

These quotations stand in marked contrast to Lothar Meyer's statement that the existence of some sixty or even more fundamentally different kinds of primordial matter is intrinsically not very probable" (1884, p. 129).

How could Mendeleev have been so wrong about reduction of the periodic system, or was he indeed wrong? Interestingly, Paneth has argued that, although in some ways Lothar Meyer turned out to be more correct on reduction, Mendeleev would not need to change his view on the basis of current knowledge:

> Yet I believe that something very essential in his fundamental philosophical tenets would have remained untouched by the progress in physics and could be successfully defended even today; and it is just these "philosophical principles of our science" which he regarded as the main substance of his textbook. (Paneth, 1965, pp. 56–57)

What Paneth had in mind is that Mendeleev adopted an intermediate position between realism and reduction to physics:

> The reduction to unity (or quadruplicity) has been successfully achieved by physics; chemistry however will probably preserve, as long as there is still a science of chemistry in the present meaning of the word, a plurality of its basic substances in complete agreement with the doctrine of its old master, Dimitri Ivanovich Mendeleeff. (Paneth, 1965, p. 70)

> Every science must decide for itself the units with which it builds, and the deepest foundation is by no means always the best for the purpose. (Paneth, 1965, p. 67)

Similarly, the French philosopher Bachelard, who began his career as a physical chemist, has written, La pensee du chimiste nous parait osciller entre le pluralisme d'une part et la reduction du pluralisme d'autre part (Bachelard, 1932).

Paneth's Own Intermediate Position: Isotopy and the New Element Scheme

Paneth is clearly not a naive realist because he recognizes two senses of the term *element*. Indeed, he is the last chemist of any note to have stressed the value in drawing this distinction.[31] In fact, Paneth's element scheme is the one still in use to this day, although most contemporary chemists would probably be loath to recognize a metaphysical or transcendental aspect to the nature of the elements, falsely believing that this might smack of alchemy, which they, of course, take to be a gravely mistaken enterprise.[32]

Even though the development of the periodic system was an unparalleled success, especially at the hands of Mendeleev, who predicted new elements and corrected the atomic weights of several existing ones, a number of problems nevertheless began to emerge. First, there was the question of the apparent inversion of the positions of the elements tellurium and iodine. If these two elements were ordered according to atomic weight, they fell into chemically incorrect groups. Mendeleev simply reversed their positions, thus putting more faith in chemical properties and believing that the atomic weights of these elements had been incorrectly measured. But many heroic attempts to show that tellurium has a lower atomic weight than iodine were completely fruitless. This reversal problem, along with a couple of others in different parts of the periodic table, were to remain unsolved for many more years.

Second, the accommodation of the rare earth elements into the periodic system was proving to be quite a challenge for Mendeleev. In broad terms, these elements have almost identical chemical properties such that one might be tempted to put them all into the same place in the periodic table, a result that would contradict the spirit of the entire classification scheme.

The third issue concerned the discovery, in 1894, of the element argon that seemed to be mysteriously devoid of the power to combine with other elements and could not initially be fitted into the periodic system. Several more gases of this type were discovered over the next few years, thus confounding the problem of their accommodation further. It cannot be denied that the discovery of this completely new group of elements, which had not been predicted by anyone, raised some concern regarding the soundness of the periodic system. In 1900 Ramsey, who had isolated these mysterious "noble gases," suggested a new column to be placed between the halogens and the alkali metals in the periodic table, a proposal that Mendeleev readily agreed to.

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But even more severe worries were looming in the distance, not just for the periodic system but for the very meaning of the concept of an element. In 1896 Becquerel discovered that certain elements decay radioactively. The intense study of such processes over the following years revealed a host of new "elements;" so many, in fact, that their discoverers scarcely paused to give them new names.[33] They included such things as uranium X and radiothorium, provisionally named after the elements from which they originated. The question naturally arose as to how these substances might be accommodated into the periodic system. An even deeper issue became evident when Rutherford showed that elements could be transmuted into quite different ones, something that only the alchemists had previously imagined possible. Mendeleev, a strong supporter of the nineteenth-century element scheme, could not accept such findings, especially transmutation, because they appeared to contradict the notion of the permanence of the elements. Finally, there was the problem of isotopy, which was eventually to lead to the resolution of some of these problems, but not before a number of scientific, and even philosophical, battles had been fought.

The phenomenon of isotopy refers to the fact that certain elements consist of more than one component (now called isotopes) which seemed, at the time of their discovery, to be impossible to separate. The first attempt to restore order to the situation was made by Soddy, who had discovered the phenomenon in 1911.[34] Soddy announced the theory of isotopy which stated that "isotopes of the same species are inseparable and belong in the same place in the periodic table." However, this new notion implied that one simple substance (something that could not be further purified) would be equivalent to two or more abstract elements in violation of the one-to-one correspondence demanded by the nineteenth-century element scheme. Some argued that isotopes might eventually prove to be separable in which case each isotope would have to be regarded as an abstract element.[35] However, for most chemical purposes, isotopy seemed to make no difference.

Then in 1913 Moseley, working in Manchester, discovered what we now call atomic number (Moseley, 1913). He began by photographing the X-ray spectrum of 12 elements, 10 of which occupied consecutive places in the periodic table. He discovered that the frequencies of features called K-lines in the spectrum of each element were directly proportional to the square of the integer representing the position of each successive element in the table. As Moseley put it, here was proof that "there is in the atom a fundamental quantity, which increases by regular steps as we pass from one element to the next." This fundamental quantity, first referred to as "atomic number" in 1920 by Ernest Rutherford, is now identified as the number of protons in the nucleus of an atom. Moseley's work provided a method that could be used to determine exactly how many empty spaces remained in the periodic table.

At about the same time, Bohr published his trilogy articles in which he introduced the quantum theory of the atom and obtained, by various means, the electronic configurations of many of the elements in the periodic system (Scerri, 1994b). In addition, he solidified the notion that the chemical properties of the elements were due to the orbiting electrons, which corresponds to the atomic charge of each nucleus (Bohr, 1913). Here, then, with the discoveries of Moseley and Bohr, was the solution of the tellurium/iodine inversion question. If the elements were ordered according to atomic

charge instead of atomic weight, then everything fell into place. Tellurium, with a lower atomic charge than iodine, could now justifiably be placed before iodine, as its chemical properties demanded it should.

However, up to this point the theory of isotopy had been based on a negative result, namely the apparent inability to separate the isotopes of a simple substance. In 1914 Paneth and von Hevesy set out to examine this notion more directly. Was it just that isotopes could not be separated and so should be regarded as belonging to the same element by default as Soddy's theory demanded, or was it that they really did share the same chemical properties?[36]

Replaceability

Paneth and his collaborator von Hevesy took the view that isotopes might be chemically identical and began to explore this notion experimentally (Paneth & von Hevesy, 1914). They proposed the concept of replaceability of isotopes—that is, they claimed that the replacement of any isotope with another one of the same species would not produce any noticeable chemical effect. They set out to verify the correctness of this view through the law of mass action. For any reaction,

$$aA + bB \leftrightarrow cC + dD$$

it can be shown that an equilibrium constant, K_c, at any given temperature, for the reaction is given by

$$K_c = [C]^c [D]^d / [A]^a [B]^b$$

where the square brackets denote the concentrations of the species A through D.[37] If the replaceability view is correct, it should be possible to take any of these concentrations as the sum of the concentrations of all the isotopes of any particular species. To estimate these concentrations Paneth and von Hevesy used electrochemical experiments and the Nernst equation,[38]

$$E = E^\circ + (RT/nF) \ln c$$

The main experiment utilized two isotopes of bismuth, $^{209}Bi^{+3}$ and $^{210}Bi^{+3}$, with the result that the observed voltage was found to be constant, regardless of the proportion of the two isotopes present in the sample, within the accuracy of the experiment. Thus, they demonstrated that replaceability was indeed an experimental fact. Isotopes of a single species[39] had been shown to be chemically indistinguishable.[40]

In 1918 Aston discovered isotopes in a number of non-radioactive elements that led to a strengthening of Paneth's case. Paneth pointed out that elements in Fajans's sense of the word seemed to be multiplying each day and were thus endangering the chemists' picture of the world. It would have been far-fetched for chemists to restructure the foundations of their science on the grounds that "elements" had turned out to be composite structures. At about this time Paneth stated clearly what had previously remained as an implicit definition of a chemical element: "A chemical element is a substance of which all atoms have the same nuclear charge" (Paneth, 1925 p. 842).

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Even at this time, however, isotopes were suspected to consist of smaller particles. Indeed, the radiochemist Fajans disagreed with Paneth and suggested that each isotope should be regarded as an element, a view, which if taken seriously, would have committed chemistry to research into elementary particles (Fajans, 1914). Chemists were not prepared for this change, nor were they motivated to abandon their existing successful research programs. In 1919 a decisive experiment was conducted by Rutherford, who succeeded in artificially decomposing the nucleus by using α particles, but the method he used could scarcely be described as chemical. Fajans was forced to demarcate between decomposition carried out by physical means (Rutherford's experiment) as opposed to chemical means, and Paneth, who had advocated such a demarcation from the start, was thus vindicated.

Paneth's New Element Scheme

Paneth then took on the more philosophical task of revising the nineteenth-century element scheme to accommodate the new findings, especially the results of his own and von Hevesy's replaceability experiments. One of his aims was to explain to chemists at large the implications of Soddy's theory, which was that chemical analysis does not proceed down to the most fundamental level, a feature that most chemists were finding rather disconcerting at this time.

Paneth was to use the positive results that emerged from the replaceability work to offer a solution. In his new element scheme a mixture of chemically inseparable isotopes was identified with a single element.[41] It will be recalled that in the nineteenth-century scheme an abstract element is a property bearer and also a material ingredient characterized by atomic weight. If Paneth was to reconcile his own element scheme with the more established nineteenth-century scheme he would have to consider the following two points: (1) whether isotopic simple substances were to be regarded as different simple substances—Paneth would answer no, because every *chemical* attempt to separate a mixture of isotopes had failed; and (2) if abstract elements combined the aspect of property bearer and material ingredient (atomic weight), what should be made of isotopes, which had different atomic weights? Would they also have to be regarded as different property bearers and so as different abstract elements? Again Paneth would answer no, but this response required a severing of the connection between the aspect of being a property bearer and also a material ingredient characterized by atomic weight. According to the replaceability experiments, Paneth reasoned that isotopes were the same property bearer but not the same material ingredient because isotopes of the same element differ in atomic weight.[42]

Now this severing of material ingredient, in the form of atomic weight, from property bearer seemed to have other consequences that Paneth also succeeded in explaining. For example, there are several laws based on atomic weight in chemistry to account for the amounts in which elements combine.[43] What would happen if atomic weight, the classical material ingredient, were to be banished from its function of characterizing an abstract element in the observable world? Paneth's response was that the chemical weight laws had already been falsified with the discovery of radioactivity. If a chemical reaction involves a radioactive substance—say A—then it is not the case that atomic

weight is conserved as in the kinds of stoichiometric problems that beginning chemistry students are made to perform:

$$A + B \rightarrow C$$

This is because A has lost some of its weight in the time it takes for this reaction to proceed and for weighing to be made. The loss of significance of atomic weight as the material ingredient of an abstract element raises the question of how chemical properties are carried so that different isotopes may show the same chemical reaction. Of course, the answer lay, in making atomic number the new material ingredient.

To summarize, Paneth's scheme retains the analytic limit characteristic of chemistry. A simple substance is one that cannot be further analyzed by *chemical* means, and a mixture of isotopes is, therefore, regarded as a single simple substance. The notion of a one-to-one correspondence between simple substance and abstract element is retained with the result that Paneth is forced to change the material ingredient from atomic weight to atomic number. The nineteenth-century connection between an abstract element as a property bearer (unobservable) and its material ingredient as atomic weight is broken once and for all.[44] In Paneth's scheme, replaceable isotopes correspond to, or are representatives of, the same abstract element. The periodic table that summarizes the properties of abstract elements is preserved instead of needing to devise a complicated new table for the individual isotopes of all the elements.

Paneth's contribution was thus to uphold the autonomy of chemistry and to resist following the reductive path of the physicist, which would have destroyed the periodic system and would eventually have turned chemistry into elementary particle physics. In fact, Paneth was recommending a form of naive realism whereby isotopes of the same element could be regarded as being identical in chemistry, even though we know that they are not strictly identical from the more reductive perspective of physics.

Throughout these developments all the major suggestions made by Paneth were vigorously opposed by Kasimir Fajans, as already mentioned here. Fajans disputed the Paneth–von Hevesy replaceability results and later criticized Paneth's elements scheme, believing that individual isotopes of any particular element should indeed be regarded as distinct simple substances and that they should also be regarded as distinct abstract elements.

Interestingly, Fajans seems to have preferred to use the terms *theoretical element* and *practical element*. Theoretical elements were truly fundamental for Fajans, whereas practical elements were those that had been shown to have resisted decomposition thus far. From the point of view of this essay, this point is significant because it emphasizes that at the beginning of the century the philosophical notion of abstract element (Paneth) or theoretical element (Fajans) was widely held. Indeed, here are two chemists who disagreed on many aspects of the new radiochemistry but took it for granted that the nature of elements consisted in a dual observable and nonobservable nature. It is doubtful whether a contemporary chemist would have arrived at Paneth's element scheme or indeed Fajans's alternative in the absence of such a philosophical appreciation of the subject matter.

The final seal of approval for Paneth's element scheme came in 1923, when a IUPAC committee met in Paneth's absence and, apart from minor differences in terminology,

adopted the proposal that he had made as early as 1916 (Aston et al., 1923). Moreover, in an influential article to *Nature* in 1919, Aston used terminology for the elements that he attributed to Paneth.

One further interesting development took place in 1932, when Urey discovered isotopes of hydrogen. In these cases, the masses of the isotopes differ from each other by as much as 100% (Urey & Grieff, 1935). The properties of these isotopes are definitely not the same. For example water (mostly protium oxide) has a boiling point of 100°C, whereas the value for deuterium oxide is 104°C. Strictly speaking, Fajans had been correct to doubt replaceability, but the problem is only significant in isotopes with very low masses, and Urey's discovery did not change the chemical definition of an element in any way.

The conclusion to be drawn from this episode is that chemistry is not obliged to accept every single step toward reduction, which may be suggested by research in physics. Whereas the concept of atomic number represents a beneficial reduction for chemists to embrace, a restructuring of the subject based on the physical difference isotopy would have led to the demise of the periodic system. As Greenaway says in an article to commemorate the 100th anniversary of Mendeleev's periodic table:

> The chief influence of the periodic table on chemistry was to turn it from endless diversification in a search for unknown compounds and elements to a concentration on order and its underlying cause. Chemistry was able to assimilate the new physics—the electron, radioactive transformation etc., without fundamental change. (Greenaway, 1969, p. 99)

The Paneth episode would seem to be another example of the chemist's need to adopt an intermediate position, which, while acknowledging the findings of the reducing science of physics, upholds the autonomy of chemistry and recognizes where to stop:

> Nowadays we know that they [the elements] are composite in two senses: they consist of a mixture of isotopes, and the atoms of every isotope are built up from simpler constituent particles. Since, however, in chemical reactions there is neither an unmixing of the isotopes nor any change in the essential parts of the atom, the law of the conservation of the elements is valid in *chemistry*.
>
> Conviction on this point permits us, in complete agreement with Mendeleeff, to regard the chemical elements as our ultimate building blocks. If we investigate the foundations of chemistry as an independent science, then indeed we do not come up against those primary qualities which for centuries were regarded as the ultimate principles in physics viz. size, shape and motion . . . neither do we encounter the four qualities of physics mentioned above . . . (the neutron, the two types of electron, and the neutrino), but only these eighty-nine chemical basic substances. (Paneth, 1965, p. 68)

Conclusion

The central message of this article, which I believe remains relevant in today's chemistry, has been that the best strategy for the chemist to adopt lies in what I call the intermediate position between reduction and varying degrees of realism. This recommendation would seem to be especially relevant to modern-day chemistry, which has looked increasingly as if it were being overrun by physics. I will now conclude by

giving a summary of the main ideas in this article, and in so doing I will attempt to restore some form of historical order to the events discussed.

Mendeleev, the creator of the periodic system of the elements, drew the philosophical distinction between basic substances (abstract elements) and simple substances. Therefore, he cannot be accused of having acted as a naive realist. However, having arrived at the periodic classification by giving emphasis to abstract elements, he resisted the prevalent reductionist tendency of supposing the existence of a primary matter. He considered the elements as distinct individuals and adopted an intermediate position between realism and reduction.

Paneth later followed Mendeleev in insisting on the distinction between basic substances and simple substances. While praising the chemist's use of naively realistic notions in most instances, Paneth pointed out that, to understand how the elements persist in the compounds, chemists must assume a more philosophical position. When faced with the question of isotopy, Paneth maintained the distinction between basic substances and simple substances but did not follow the reductive path of the physicist who would have been inclined to regard isotopes as different elements. Thus Paneth adopted an analogous intermediate position to that of Mendeleev.

In contemporary chemistry, concepts such as orbitals, configurations, and hybridization are frequently used as though they were "real," contrary to the pronouncements of modern physics and philosophers of science who deny the reduction of such typically chemical concepts to quantum mechanics. In this case, the realism I am identifying takes the form of an unwarranted belief in microscopic entities that the theory tells us do not, in fact, exist. My claim is that modern chemistry correctly continues to adopt an intermediate position between realism and reduction in the tradition of Mendeleev and Paneth.

Notes

1. Scerri (1991a, 1991b, 1994a, 1995, 1997a, 1997c, 1998a).

2. Heinz Paneth changed his last name to Post sometime around 1953.

3. Post founded the department of history and philosophy of science at what was then Chelsea College, London University, and which subsequently merged with King's College, London. He has also been one of the most influential postwar philosophers of science in Great Britain. His father, Fritz Paneth, one of the founders of radiochemistry, had a deep interest in philosophical aspects of chemistry, as can be seen in his collected essays (Paneth, 1965).

4. In philosophy, the term *naive realism* is generally taken to mean a belief in macroscopic objects for what they appear to be and independently of any views on what lies below the surface. I will be using the term in this sense but will also use it to mean the adoption of superficial views about microscopic entities when discussing atomic orbitals and configurations.

5. In the case of the hydrogen atom an atomic orbital is well defined in the sense that four quantum numbers can be genuinely attributed to the one electron.

6. If reduction of chemistry as a whole is considered from a naturalistic viewpoint as I have advocated previously (Scerri, 1998a), the question of whether or not chemistry has been reduced to quantum mechanics is more subtle and depends on the present state of computational quantum chemistry and in particular ab initio calculations of chemical properties. In this sense, one might want to concede that chemistry has been approximately reduced to

quantum mechanics, although even the notion of approximate reduction is problematical (Scerri, 1994a).

7. However, the main focus of this chapter is not on the issue of realism, and so I will not be concerned with such issues as warrants for belief.

8. An even more asymmetrical aspect concerns the precise placement of the rare earth element block, which in many tables is still shown to begin one element to the right of the start of the d block. This is despite the fact that several articles have pointed out that the f block truly belongs between the s and d blocks (Jensen, 1986).

9. The f block refers to the rare earth elements. The label f originally stood for the fundamental lines in the spectrum.

10. I am not suggesting that the medium–long form originated with quantum mechanics. Indeed, early versions of this kind were suggested by Werner among others (Werner, 1905).

11. See van Spronsen (1969) and Mazurs (1974) for other pyramidal forms of the table.

12. Of course, there is another pragmatic reason why the medium–long form rather than the pyramidal form has gained widespread acceptance and that is the fact that chemical groups are very easily seen as vertical columns in the medium–long form whereas they are not quite so easily noticed in the pyramid form, although the connecting lines serve to reinforce the group connections.

13. I do not exclude the possibility that future advances may lead to a strict deduction of the points at which the periods close. Similarly, a future generalization of quantum mechanics might enable one to explain the closing of the periods from first principles.

14. The notion of abstract elements is a recurring theme in the remainder of this chapter.

15. The reader will not be surprised to learn that Paneth was familiar with Kant's philosophical views.

16. For a discussion of this point, see Paneth's 1962 article. Also, the mere fact that Mendeleev, and considerably later Paneth, continue to maintain a dual nature for the elements attests to the fact that the chemical revolution did not eliminate the metaphysical view.

17. However, Paneth argues that Mendeleev was somewhat confused in the terminology he chose to discuss this issue. Mendeleev makes the distinction between simple bodies and elements in several passages: "A simple body is something material, for example a metal or metalloid, endowed with physical properties and the ability to show chemical reactions. To the concept of the simple body corresponds the molecule consisting of several atoms . . . On the other hand, element is a term for those material constituent parts of simple and composite bodies which determine their physical and chemical behavior. The concept corresponding to element is the atom". (Paneth, 1871, p. 141). Paneth claims that this is an error on Mendeleev's part. While agreeing that the distinction is a very important one, he believes that the reason it has received so little attention is that the terms used by Mendeleev are not very appropriate. One cannot introduce a distinction between element and simple body since, according to Lavoisier, the definition of element IS a simple body. Second, Paneth thinks that by the association of the terms *element* with *atom* and *simple body* with *molecule*, respectively, Mendeleev seems to have missed the essential point (Paneth, 1965, p. 57). This is because atoms and molecules belong to the same group of scientific concepts, or the same category of concepts, while the fundamental difference which Mendeleev intends to draw between element and simple body is due to their belonging to entirely different epistemological categories.

18. E.R. Scerri & J.W. Worral "Prediction and the Periodic Table", (to appear).

19. For example, see Leicester 1948).

20. If one insists on calling it a metaphysical position, it must be made clear that it is intended in the literal sense of the word, meaning beyond the physical and not the modern philosophical meaning or indeed the Aristotelian sense of the term, meaning what actually exists fundamentally. As is well known, Aristotle's famous book on the subject merely came

after his physics, and this is where modern metaphysics gets its name. Aristotle's book was not called metaphysics because it was intended as an investigation into what lies beyond physics or beyond observation.

21. Such caution began to fade toward the end of the nineteenth-century to the extent that simple substances that had been isolated began to be regarded as the only form of an element and the abstract counterpart to each simple substance was largely forgotten.

22. The more prosaic explanation given in contemporary chemistry is that what survives of each of the elements is the number of protons—in other words, the nuclear charge of the atoms of sodium and chorine. This would also be the case in rather extreme examples such as the Na^{+11} and Cl^{+17} ions. Although this response is surely correct, it also seems a little unsatisfactory
for the identity of chemical elements to depend on the nucleus of their atoms, given that all the chemical properties are supposed to be determined by the configurations and exchanges in the electrons around the nucleus. This paradox has also recently been noted by Noretta Koertge (Koertge, 1998).

23. This is perhaps why Mendeleev, a great defender of the nineteenth-century element scheme, was so reluctant to accept the notion of the transmutation of the elements discovered by Rutherford at the turn of the twentieth-century.

24. Indestructible in the sense that weights are conserved in the course of chemical reactions. This was, of course, the basis of the chemical revolution of Lavoisier.

25. This is despite the fact that our present element scheme, which we owe to Paneth, was arrived at partly by his insistence on the distinction between abstract element and simple substance, as will be discussed later.

26. Of course, I do not mean to imply that the weights of individual atoms can be directly observed. I intend this remark in the chemist's sense that stoichiometric reactions can be rationalized by appeal to atomic weights of participating elements.

27. Mendeleev correctly revised the atomic weight of uranium from 120 to 240. He also predicted intuitively that tellurium should be placed before iodine, thus ignoring the atomic weight ordering for these elements.

28. Whether or not Mendeleev was influenced by Kant's philosophical writings is an issue I will take up in a forthcoming study.

29. A detailed discussion of predictions and the periodic system is given in van Spronsen, (1969). See especially chapter 7.

30. Mention might also be made of the new journal *Foundations of Chemistry* published by Kluwer.

31. The 1962 article is a translation of a lecture given by Paneth in 1931 to the Gelehrte Gesellschaft of Königsberg.

32. For a healthy antidote to this generally held negative view of alchemy, see Pierre Laszlo's "Circulation of Concepts" (1999).

33. As Badash has written, by 1913 over 30 radioelements were known, but there were only 12 places in the periodic table in which to place them" (Badash, 1979).

34. Isotopy was only found in radioactive elements, but in 1913 J.J. Thomson also discovered the effect in the nonradioactive element neon. This was soon shown to be a perfectly general result. Many elements occur as two or more isotopes, although a number of elements only possess a single isotopic form.

35. In fact, isotopes were separated by Aston in 1919, but this fact did not affect Paneth's new element scheme, which became generally adopted, and formed the basis for the definition of the term element by IUPAC in 1923.

36. It would appear that Paneth and von Hevesy were following a rather Popperian strategy.

37. Strictly speaking, the relationship is valid for the activities of substances A to D. In the case of dilute solutions, activities can be equated with concentrations.

38. Where E is the potential of a half-cell, E° is the standard electrode potential, R the ideal gas constant, T the absolute temperature, n the number of electrons transferred in the course of the half reaction, F the Faraday constant, and c the concentration of the dissolved species.

39. The word *element* has not been used here because this is precisely the issue being addressed. Are we, in fact, dealing with one "element" or more?

40. Another leading radiochemist, Kasimir Fajans, objected to the interpretation of these results on the basis of a thermodynamic analysis and put forward the view that isotopes are different, not just physically but also chemically (Fajans, 1914). Various other experiments were then devised and carried out in an attempt to settle the issue, but the debate continued and, indeed, was widened to the question of what constitutes a chemical element.

41. This was in keeping with Soddy's theory, but, it was now being expressed in more positive terms based on experimental findings.

42. He accommodated the fact that different isotopes have different radioactive properties (typically different half-lives if they are radioactive) by stating that these would not count as chemical properties.

43. This issue is discussed in Kultgen's 1958 article, as well as in most chemistry textbooks.

44. Paneth concluded that if atomic weight was causing problems in this context it was because it was not a chemical property. Since the time of Newton, substances or bodies had become characterized by their weight. This view gained greater acceptance when first Lavoisier and then Dalton emphasized the need to characterize different chemical substances according to weight. refers to S. Toulmin in *Encyclopedia of Philosophy* (Toulmin, 1967).

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ERIC R. SCERRI

JUST HOW AB INITIO IS AB INITIO QUANTUM CHEMISTRY? *

1. INTRODUCTION

Quantum Mechanics has been the most spectacularly successful theory in the history of science. As is often mentioned the accuracy to which the gyromagnetic ratio of the electron can be calculated is a staggering nine decimal places. Quantum Mechanics has revolutionized the study of radiation and matter since its inception just over one hundred years ago. The impact of the theory has been felt in such fields as solid state physics, biochemistry, astrophysics, materials science and electronic engineering, not to mention chemistry, the subject of this conference.

Quantum Mechanics offers the most comprehensive and most successful explanation of many chemical phenomena such as the nature of valency and bonding as well as chemical reactivity. It has also provided a fundamental explanation of the periodic system of the elements that summarizes a vast amount of empirical chemical knowledge. Quantum Mechanics has become increasingly important in the education of chemistry students. The general principles provided by the theory mean that students can now spend less time memorizing chemical facts and more time in actually thinking about chemistry.

I hope that with these opening words I have succeeded in convincing the audience that I do not come before you to deny the power and influence of Quantum Mechanics in the field of chemistry.

* A previous version of this article appeared as 'Löwdin's Remarks on the Aufbau Principle and a Philosopher's View of Ab Initio Quantum Chemistry' in E.J. Brändas, E.S. Kryachko (Eds.) *Fundamental World of Quantum Chemistry*, Vol. II, 675–694, Kluwer, Dordrecht, 2003.

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2. THE AIM OF THIS WORK

My project is somewhat different. With the triumph of quantum mechanics there has been an inevitable tendency to exaggerate its success, especially on the part of practicing quantum chemists and physicists. As a philosopher of chemistry I have the luxury of being able to examine the field as an outsider and of asking the kinds of questions which true practitioners might not even contemplate.

Quantum mechanics is part of the reductionist tradition in modern science, and the general claim, often just made implicitly as in any branch of reduction, is that the highest ideal one can aspire to is to derive everything from the theoretical principles. The less experimental data one needs to appeal to, the less one is introducing measured parameters the purer the calculation and the closer it approaches to the ideal of Ockham's razor of being as economical as possible (Hoffmann et al., 1996).

Of course there is no such thing as a completely *ab initio* calculation and if one looks far enough back at the history of any scientific theory one finds that it began with the assumption of at least some experimental data. But it is also fair to say that once the basic principles of a theory have been arrived at, the theorist may 'kick away' the historical-experimental scaffolding. The modern student of quantum mechanics, for example, is not obliged to follow the tortuous route taken by Planck, Einstein, De Broglie, Schrödinger and others. She can go directly to the postulates of quantum mechanics where she will find procedures for doing all kinds of calculations and she can safely ignore the historical heritage of the theory. Indeed many argue, and correctly in my view, that it is actually a hindrance for the practitioner to get too involved in the historical aspects of the theory although it may of course be culturally enriching to do so.

The epitome of the ab initio approach is something like Euclidean geometry where one begins with a number of axioms and one derives everything from this starting point without any recourse whatsoever to empirical data. Needless to say geometry, Euclidean or otherwise, has its origins in the dim distant past when agrarian man needed to think about lines and angles and areas of land. But once the concepts of line, angle and distance had been sufficiently abstracted the agrarian heritage could be completely forgotten.

In a similar way my question today is going to be to ask to what extent the periodic table of the elements can be *explained* strictly from first principles of quantum mechanics without assuming any experimental data whatsoever. I suspect that some physicists and chemists in the audience might well experience some irritation at the almost perverse demands which I will make on what should be derivable from the current theory. If so then I apologize in advance.

By adopting a perspective from the philosophy of science we will cross levels of complexity from the most elementary explanations based on electron shells to frontier ab initio methods. Such a juxtaposition is seldom contemplated in the chemical literature. Textbooks provide elementary explanations that necessarily distort the full details but allow for a more conceptual or qualitative grasp of the main ideas. Meanwhile the research literature focuses on the minute details of particular methods or particular chemical systems and does not typically examine the kind of explanation that is being provided. To give a satisfactory discussion of explanation in the context of the periodic table we need to consider both elementary and supposedly deeper explanations within a common framework.

One of the virtues of philosophy of science is that it can bridge different levels in this way since it primarily seeks the 'big picture' rather than the technical details. In fact supposedly elementary explanations often provide this big picture in a more direct manner but what is also needed is to connect the elementary explanation to the technical details in the deeper theories.

The question of whether or not different levels of explanation for any particular scientific phenomenon are in fact consistent and whether they form a seamless continuum has been the subject of some debate. For example in her first book Nancy Cartwright goes to some lengths to argue that many different explanations can be found for the action of lasers and suggests that these explanations are not necessarily consistent with each other (Cartwright, 1983). In other writings she has expressed some support for the thesis that the various special sciences are dis-unified (Cartwright, 1996).

My own view differs from Cartwright's in that I am of the opinion that the sciences are unified and that explanations given for the same scientific phenomenon at different levels are essentially consistent, although the connection if frequently difficult to elaborate in full

(Scerri, 2000). In this paper I will attempt to draw such connections for the various explanations of the periodic table given at different levels of sophistication.[1]

3. FIRST AN ELEMENTARY APPROACH

Let us start at an elementary level or with a typically 'chemical' view. Suppose we ask an undergraduate chemistry student how quantum mechanics explains the periodic table. If the student has been going to classes and reading her book she will respond that the number of valency or outer-shell electrons determines, broadly speaking, which elements share a common group in the periodic table. The student might possibly also add that the number of outer-shell electrons *causes* elements to behave in a particular manner.

Suppose we get a little more sophisticated about our question. The more advanced student might respond that the periodic table can be explained in terms of the relationship between the quantum numbers which themselves emerge from the solutions to the Schrödinger equation for the hydrogen atom.[2]

This more sophisticated explanation for the periodic system is provided in terms of the relationship between the four quantum numbers that can be assigned to any electron in a many-electron atom. The first quantum number n can adopt any integral value starting with 1. The second quantum number which is given the label ℓ can have any of the following values related to the values of n,

$$\ell = n - 1, \ldots 0$$

In the case when n = 3 for example, ℓ can take the values 2, 1 or 0. The third quantum number labeled m_ℓ can adopt values related to those of the second quantum numbers by the relationship,

$$m_\ell = -\ell, -(\ell + 1), \ldots 0 \ldots (\ell - 1), \ell$$

For example if $\ell = 2$ the possible values of m_ℓ are,

$$-2, -1, 0, +1, +2$$

Finally, the fourth quantum number labeled m_s can only take two possible values, either +1/2 or −1/2 units of spin angular

momentum. We thus have a hierarchy of related values for the four quantum numbers, which are used to describe any particular electron in an atom. These relationships are derived theoretically and do not involve the use of any experimental data.[3]

For example, if the first quantum number is 3 the second quantum number ℓ can take values of 2, 1 or 0. Each of these values of ℓ will generate a number of possible values of m_ℓ and each of these values will be multiplied by a factor of two since the fourth quantum number can adopt values of 1/2 or $-1/2$. As a result there will be a total of $2 \times (3)^2$ or 18 electrons in the third shell. This scheme thus explains *why* there will be a maximum total of 2, 8, 18, 32 etc. electrons in successive shells as one moves further away from the nucleus.

4. HOW DOES THIS EXPLAIN THE FORM OF THE PERIODIC TABLE?

But does the fact that the third shell can contain 18 electrons also explain why some of the periods in the periodic system contain eighteen places? Actually not exactly. If electron shells were filled in a strictly sequential manner there would be no problem and the explanation would in fact be complete. But as anyone who has studied high school chemistry is aware, the electron shells do not fill in the expected sequential manner. The configuration of element number 18, or argon is,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$

This might lead one to think that the configuration for the subsequent element, number 19, or potassium, would be

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^1$$

since up to this point the pattern has been to add the new electron to the next available orbital in the sequence of orbitals at increasing distances from the nucleus. However experimental evidence shows quite clearly that the configuration of potassium should be denoted as,

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

As many textbooks state this fact can be explained from the fact that the 4s orbital has a lower energy than the 3d orbital. In the case of element 20 or calcium the new electron also enters the 4s orbital and for the same reason.

5. TRANSITION METAL CONFIGURATIONS

The interesting part is what happens next. In the case of the next element, number 21, or scandium, the orbital energies have reversed so that the 3d orbital has a lower energy, as shown in Figure 1. Textbooks almost invariably claim that since the 4s orbital is already full there is no choice but to begin to occupy the 3d orbital. This pattern is supposed to continue across the first transition series of elements, apart from the elements Cr and Cu where further slight anomalies are believed to occur.

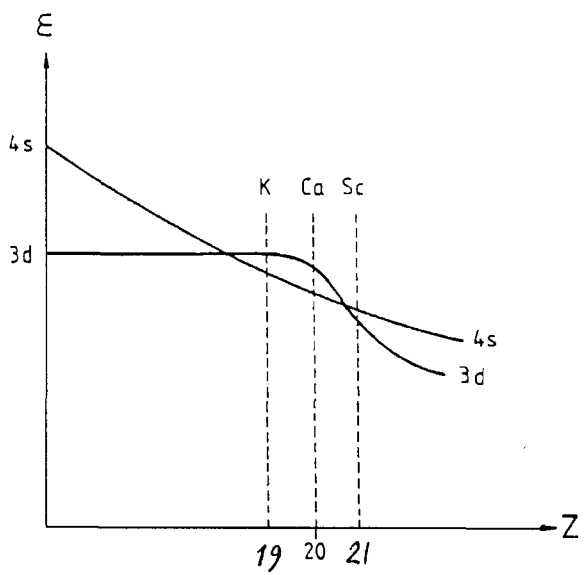

Figure 1. Variation of 4s and 3d orbital energies as a function of Z, atomic number.

In fact this explanation for the configuration of the scandium atom and most other first transition elements is inconsistent. If the 3d orbital has a lower energy than 4s starting at scandium then if

TABLE I

Table of configurations of first transition series

Sc	Ti	V	Cr	Mn	Fe
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$
	Co	Ni	Cu	Zn	
	$4s^23d^7$	$4s^23d^8$	$4s^23d^9$	$4s^13d^{10}$	

one were really filling the orbitals in order of increasing energy one would expect that all three of the final electrons would enter 3d orbitals. The argument which most textbooks present is incorrect since it should be possible to predict the configuration of an element from a knowledge of the order of its own orbital energies (Scerri, 1989; Vanquickenborne et al., 1994). It is incorrect to consider the configuration of the previous element and assume that this configuration is carried over intact on moving to the next element, especially in cases where orbital energies cross over each other as they do in this case. It should be possible to predict the order of orbital filling for the scandium atom on its own terms. If one tries to do so, however, one predicts a configuration ending in $3d^3$, contrary to the experimental facts.

The full explanation of why the $4s^23d^1$ configuration is adopted in scandium, even though the 3d level has a lower energy, emerges from the peculiarities of the way in which orbital energies are defined in the Hartree–Fock procedure. The details are tedious but have been worked out and I refer anyone who is interested in pursuing this aspect to the literature (Melrose and Scerri, 1996).[4]

6. HOW ARE CONFIGURATIONS DERIVED FROM THE THEORY?

But let me return to the question of whether the periodic table is fully and deductively explained by quantum mechanics. In the usually encountered explanation one assumes that at certain places in the periodic table an unexpected orbital begins to fill as in the case of potassium and calcium where the 4s orbital begins to fill before the 3d shell has been completely filled (Scerri, 1989). This information itself is not derived from first principles. It is justified *post facto* and

TABLE II

Calculated energy levels for two scandium atom configurations

Sc	$4s^2 3d^1$		
	Non-Relativistic	−759.73571776	(atomic units or Hartrees)
	Relativistic	−763.17110138	
	$4s^1 3d^2$		
	Non-Relativistic	−759.66328045	
	Relativistic	−763.09426510	

by some very tricky calculations at that (Melrose and Scerri, 1997; Vanquickenborne et al., 1994).

But if we ignore the conceptual paradox of why 4s fills preferentially even though it has a higher energy than 3d we can just concentrate on calculations aimed at determining the ground state configuration. Suppose we were to use the most widely used method for calculating the energies of atoms and molecules in an ab initio fashion. The Hartree–Fock method[5] can be used to compare the energies of the scandium atom with two alternative configurations,

$$[Ar]4s^2 3d^1 \quad \text{and} \quad [Ar]4s^1 3d^2$$

This can be carried out using ordinary non-relativistic quantum mechanics or alternatively by including relativistic effects. The results of using a readily available program on the Internet, created by Froese Fischer[6] one of the leaders in the field of Hartree–Fock calculations, shown in Table II (http://hf5.vuse.vanderbilt.edu/hf.html).[7]

In each case the more negative the calculated value of the energy the more stable the configuration. Clearly the inclusion of relativistic effects serves to reduce the energy from the non-relativistic value. In the case of scandium it appears that both non-relativistic and relativistic *ab initio* calculations correctly compute that the $4s^2$ configuration has the lowest energy in accordance with experimental data. But these calculations, including the ones for subsequent elements must be done on a case-by-case basis. There is not yet a general derivation of the formula which governs the order of filling, sometimes called the $n + \ell$, or Madelung rule, which states that given

TABLE III

Calculated energy levels for two chromium atom configurations

Cr	$4s^1 3d^5$	
	Non-Relativistic	−1043.14175537
	Relativistic	−1049.24406264
	$4s^2 3d^4$	
	Non-Relativistic	−1043.17611655
	Relativistic	−1049.28622286

a choice of filling any two orbitals the order of filling goes according to increasing values of $n + \ell$. For example, 4s where $n + \ell = 4$, fills before 3d where $n + \ell = 5$. But similar calculations do not fare as well in other atoms. Consider the case of the chromium atom for example.

It appears that both non-relativistic and relativistic calculations fail to predict the experimentally observed ground state which is the $4s^1 3d^5$ configuration, as seen in Table III. Of course I do not deny that if one goes far enough in a more elaborate calculation then eventually the correct ground state will be recovered. But in doing so one knows what one is driving at, namely the experimentally observed result. This is not the same as strictly predicting the configuration in the absence of experimental information. In addition, if one goes beyond the Hartree–Fock approximation to something like the configuration interaction approach there is an important sense in which one has gone beyond the picture of a certain number of electrons in a set of orbitals.[8] Rather than just having every electron in every possible orbital in the ground state configuration we now have every electron in every one of thousands or even millions of configurations each of which is expressed in terms of orbitals.

7. COPPER ATOM

Let me consider the case of the copper atom calculated to the same degree of accuracy via the Hartree–Fock method. For this atom the experimentally observed ground state configuration is $4s^1 3d^{10}$.

TABLE IV

Calculated energy levels for two copper atom configurations

Cu	$4s^1 3d^{10}$	
	Non-Relativistic	−1638.96374169
	Relativistic	−1652.66923668
	$4s^2 3d^9$	
	Non-Relativistic	−1638.95008061
	Relativistic	−1652.67104670

From Table IV, we see that sometimes a non-relativistic calculation gives the correct result ($4s^1 3d^{10}$), in terms of which configuration has the lower energy, and yet carrying out the calculation to a greater degree of accuracy by including relativistic effects, gives the wrong prediction. Relativistically one predicts the opposite order of stabilities than what is observed experimentally. Clearly some observed electronic configurations cannot yet be successfully calculated from first principles, at least at this level of approximation. The fact that copper has a $4s^1 3d^{10}$ configuration rather than $4s^2 3d^9$ is an experimental fact. Similarly it is from experimental data that the lengths of the periods are known and not from ab initio calculations.

The development of the period from potassium to krypton is not due to the successive filling of 3s, 3p and 3d electrons but due to the filling of 4s, 3d and 4p. It just so happens that both of these sets of orbitals are filled by a total of 18 electrons.

As a consequence the explanation for the form of the periodic system in terms of how the quantum numbers are related is semi-empirical since the order of orbital filling is obtained from experimental data. Consider now the cumulative total number of electrons which are required for the filling successive shells and periods, respectively,

Closing of shells,
Occurs at Z = 2, 10, 28, 60, 110 (cumulative totals)

Closing of periods,
Occurs at Z = 2, 10, 18, 36, 54, etc.

It is the second sequence of Z values which really embodies the periodic system and not the first. For all we know, electron shells may not even exist or may be replaced by some other concept in a future theory. But the fact that chemical repetitions occur at Z = 3, 11 and 19, if we focus on the alkali metals, for example are chemical facts which will never be superceded.

Only if shells filled sequentially, which they do not, would the theoretical relationship between the quantum numbers provide a purely deductive explanation of the periodic system. The fact that the 4s orbital fills in preference to the 3d orbitals is not predicted in general for the transition metals but only rationalized on a case by case basis as we have seen. In some cases the correct configuration cannot even be rationalized, as in the cases of chromium and copper, at least at this level of approximation. Again, I would like to stress that whether or not more elaborate calculations finally succeed in justifying the experimentally observed ground state does not fundamentally alter the overall situation.[9]

To sum-up, we can to some extent recover the order of filling by calculating the ground state configurations of a sequence of atoms but still nobody has deduced the $n + \ell$ rule from the principles of quantum mechanics. Perhaps this should be a goal for quantum chemists and physicists if they are really to explain the periodic system in terms of electronic configurations of atoms in ab initio fashion.

8. NICKEL ATOM

The case of nickel turns out to be interesting for a different reason. According to nearly every chemistry and physics textbook the configuration of this element is given as

$$4s^2 3d^8$$

However the research literature on atomic calculations (e.g., Bauschlicher et al., 1988) always quotes the configuration of nickel as

$$4s^1 3d^9$$

TABLE V

Quantum mechanical calculations for the nickel atom

Ni	$4s^2 3d^8$	
	Non-Relativistic	−1506.87090774
	Relativistic	−1518.68636410
	$4s^1 3d^9$	
	Non-Relativistic	−1506.82402795
	Relativistic	−1518.62638541

The difference occurs because in more accurate work one considers the average of all the components arising from a particular configuration and not just the lowest possible component of the ground state term. Nickel is somewhat unusual in that although the lowest energy term arises from the $4s^2 3d^8$ configuration it turns out that the average of the energies of all the components arising from this configuration lies higher in energy than the average of all the components arising from the configuration of $4s^1 3d^9$. As a consequence the $4s^2 3d^8$ configuration is regarded as the ground state in research work and it is this average energy which is compared with experimental energies as in Table V. When this comparison is carried out it emerges that the quantum mechanical calculation using either a non-relativistic or a relativistic Hartree–Fock approach gives the wrong ground state.

Of course the calculations can be improved by adding extra terms until this failure is eventually corrected. However, these additional measures are only taken after the facts are known. In addition, the lengths to which theoreticians are forced to go to in order to obtain the correct experimental ordering of terms does not give one too much confidence in the strictly predictive power of quantum mechanical calculations in the context of the periodic table. For example, the very accurate calculations on nickel include the use of basis sets which extend up to 14s, 9p, 5d as well as f orbitals (Raghavachari and Trucks, 1989).[10]

9. CHOICE OF BASIS SET

There is yet another general problem which mars any hope of claiming that electronic configurations can be fully predicted theoretically and that quantum mechanics thus provides a purely deductive explanation of what was previously only obtained from experiments. In most of the configurations we have considered, with the exception of cases mentioned above, it has been possible to use a quantum mechanical method to calculate that this particular configuration does indeed represent the lowest energy possibility. However, in performing such calculations the candidate configurations which are subjected to a variation procedure are themselves obtained from the aufbau principle and other rules of thumb such as Hund's principle or by straightforward appeal to experimental data.

There is a very simple reason for this state of affairs. The quantum mechanical calculations on ground state energies involve the initial selection of a basis set, which in its simplest, or minimal, form is the electronic configuration of the atom in question. Quantum mechanical calculations are not capable of actually generating their own basis sets that must instead be put in 'by hand'. So whereas the correct ground state electronic configurations can in many cases be selected among a number of plausible options, the options themselves are not provided by the theory. I suggest this is another weakness of the present claims to the effect that quantum mechanics explains the periodic system and it is an aspect that might conceivably corrected by future developments.

I will now attempt to take stock of the various senses of the claim that the periodic system is reduced, or fully explained, by quantum mechanics and to extend the scope of this work to more elaborate theoretical approaches.

10. QUALITATIVE EXPLANATION OF PERIODIC TABLE IN TERMS OF ELECTRONS IN SHELLS

The usually given 'explanation' for the period table takes a qualitative form. In broad terms the approximate recurrence of elements after certain regular intervals is explained by the possession of a certain number of outer-shell electrons. This form of explanation

appears to be quantitative to some people because it deals in number of electrons but in fact turns out to be rather qualitative in nature. It cannot be used to predict quantitative data on any particular atom with any degree of accuracy.

Whereas the crude notion of a particular number of electrons in shells or orbitals does not produce very accurate calculations the process can be refined in several ways. The first refinement is perhaps the use of the Hartree method of calculating self-consistent orbitals while at the same time minimizing the energy of the atom.[11] The next refinement lies in making the method consistent with the notion that electrons are indistinguishable. This requirement is met by performing a permutation of all the electrons in the atom so that each electron finds itself simultaneously in all occupied orbitals at once. It is represented mathematically as a determinant that includes all possible permutations within it.

The third refinement is to include any number of excited state configurations for the atom, in a procedure called configuration interaction or the C.I. method. One now has a sum of determinants each of which represents a particular configuration and which is included in the overall atomic wavefunction with a particular weighting determined by a coefficient which is multiplied by the appropriate determinant.

$$\Psi = c_1 D_1 + c_2 D_2 + \ldots$$

The calculation consists in finding the optimum weighting which all the determinants must have in order to minimize the energy of the atom. Having reached this level of abstraction we have really left behind the homely picture of electrons in particular shells. If one still insists on visualization, each electron is now in every orbital of every single configuration that we choose to consider.

Clearly there is still a connection with the elementary homely model but it is also fair to say that the move towards greater abstraction has somewhat invalidated the naïve model. This now raises the question as to whether the elementary model really does have explanatory power. I would argue that it does not. It may have led historically to these more sophisticated approaches but it has been rendered vastly more abstract in the process.

But if we are considering the general question of explanation it is not essential to retain the homely picture that can be grasped by the

general chemist or the beginning student of physical chemistry. We must move on to enquire about how the more abstract approaches actually fare. The short answer is much better but still not in strictly ab initio fashion.

11. NECESSARY AND SUFFICIENT CONDITIONS

But in any case even within the elementary model it emerges that the possession of a particular number of outer-shell electrons is neither a necessary nor a sufficient condition for an element's being in any particular group. It is possible for two elements to possess exactly the same outer electronic configuration and yet not to be in the same group of the periodic system. For example, the inert gas helium has two outer-shell electrons and yet is not usually placed among the alkaline earth elements such as magnesium, calcium or barium, all of which also display two outer-shell electrons.[12] The possession of a particular number of outer-shell electrons is therefore not sufficient grounds for placing it in a particular group.

Conversely, there are cases of elements that do belong in the same group of the periodic table even though they do not have the same outer-shell configuration. In fact this occurrence is rather common in the transition metal series. To take one interesting example,[13] consider the nickel group in which no two elements show the same outer shell configuration!

Ni	[Ar] $4s^2 3d^8$
Pd	[Kr] $4s^0 3d^{10}$
Pt	[Xe] $4s^1 3d^9$

In addition the very notion of a particular number of electrons in a particular shell stands in strict violation of the Pauli Principle, arguably one of the most powerful principles in the whole of science. This states that electrons cannot be distinguished, which implies that we can never really state that a particular number belong in one shell and another number in a different shell, although there is no denying the usefulness of making this approximation. The independent-electron approximation, as it is known, represents one of the central

paradigms in modern chemistry and physics and of course I am not denying its usefulness but am focusing on its ontological status.

But all this talk of electrons in shells and orbitals is just naïve realism. The lesson from quantum mechanics is the need to abandon naïve realism, to abandon picturing waves or particles or picturing spinning electrons.[14] The standard, or Copenhagen, interpretation of quantum mechanics urges us to just do the mathematics and adopt an instrumental approach to the theory. Of course this is hard especially for chemists since most of their work consists in shapes, structures, diagrams, pictures, representations and observable changes. Let us finally consider explanations of the periodic table that do not involve picturing electrons in shells or orbitals.[15]

12. AB INITIO CALCULATIONS BASED ON WAVEFUNCTIONS

Some of the more abstract ab initio approaches have already been described above. They are the Hartree–Fock method and the configuration interaction approach.

Indeed, such approaches fare much better, and are serious contenders for the claim to a full explanation of the periodic system. In order to illustrate both the power and the pitfalls of the methods I will focus for simplicity on the ab initio calculation of ionization energies of atoms. In this approach the notion of electrons in shells is used instrumentally with the knowledge that such an approximation only represents a first order approach to calculations. If one is doing a Hartree–Fock calculation then all the electrons are simultaneously in all the orbitals of a particular chosen configuration. As mentioned earlier this results from the permutation procedure. If one is doing C.I. then many thousands if not millions of configurations are considered in the wavefunction expansion.

Within these ab initio approaches the fact that certain elements fall into the same group of the periodic table is not explained by recourse to the number of outer-shell electrons. The explanation lies in calculating the magnitude of a property such as the first ionization energy and seeing whether the expected periodicity is recovered in the calculations. Figure 2 below shows schematically the experimental ionization energies for the first 53 elements in the periodic table, along with the values calculated using ab

initio quantum mechanical methods. As can readily be seen, the periodicity is captured remarkably well, even down to the details of the sections of the graph occurring between elements in groups II and III in each period of the table. Clearly the accurate calculation of atomic properties can be achieved by the theory. The quantum mechanical explanation of the periodic system within this approach represents a far more impressive achievement than merely claiming that elements fall into similar groups because they share the same number of outer-electrons.

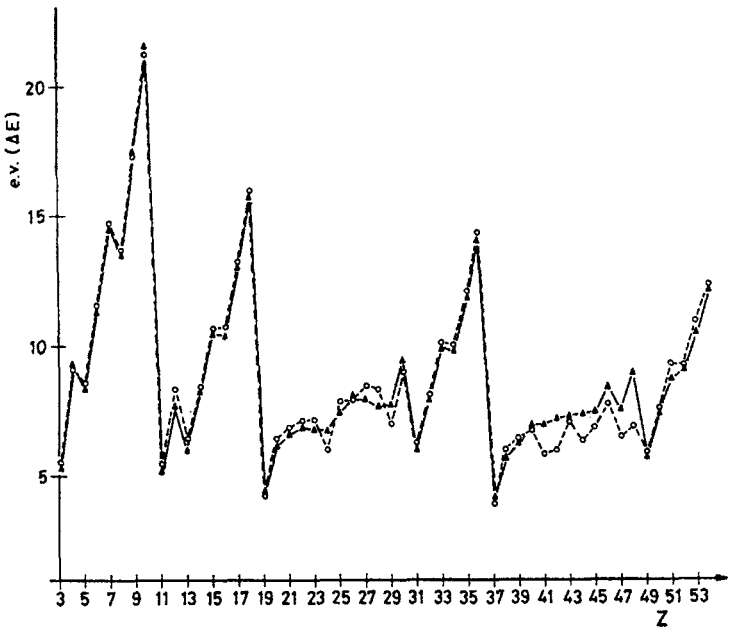

Figure 2. Comparison of computed and experimental first ionization energies for Z = 1–53.

And yet in spite of these remarkable successes such an ab initio approach may still be considered to be semi-empirical in a rather specific sense. In order to obtain calculated points shown in Figure 2 the Schrödinger equation must be solved separately for each of the 53 atoms concerned in this study. The approach therefore represents a form of 'empirical mathematics' where one calculates 53 individual Schrödinger equations in order to reproduce the well-known

pattern in the periodicities of ionization energies. It is as if one had performed 53 individual experiments, although the 'experiments' in this case are all iterative mathematical computations. This is still therefore not a general solution to the problem of the electronic structure of atoms.

13. DENSITY FUNCTIONAL APPROACH

In 1926 the physicist Llewellyn Thomas proposed treating the electrons in an atom by analogy to a statistical gas of particles. No electron-shells are envisaged in this model which was independently rediscovered by Italian physicist Enrico Fermi two years later, and is now called the Thomas–Fermi method.[16] For many years it was regarded as a mathematical curiosity without much hope of application since the results it yielded were inferior to those obtained by the method based on electron orbitals. The Thomas–Fermi method treats the electrons around the nucleus as a perfectly homogeneous electron gas. The mathematical solution for the Thomas–Fermi model is 'universal', which means that it can be solved once and for all. This should represent an improvement over the method that seeks to solve Schrödinger equation for every atom separately. Gradually the Thomas–Fermi method, or density functional theories, as its modern descendants are known, have become as powerful as methods based on orbitals and wavefunctions and in many cases can outstrip the wavefunction approaches in terms of computational accuracy.

There is another important conceptual, or even philosophical, difference between the orbital/wavefunction methods and the density functional methods. In the former case the theoretical entities are completely unobservable whereas electron density invoked by density functional theories is a genuine observable. Experiments to observe electron densities have been routinely conducted since the development of X-ray and other diffraction techniques (Coppens, 2001).[17] Orbitals cannot be observed either directly, indirectly or in any other way since they have no physical reality, a state of affairs that is dictated by quantum mechanics (Scerri, 2000). Orbitals as used in ab initio calculations are mathematical figments that exist, if anything, in a multi-dimensional Hilbert space.[18] Electron density

is altogether different, as I have indicated, since it is a well-defined observable and exists in real three-dimensional space a feature that some theorists point to as a virtue of density functional methods.[19]

14. DENSITY FUNCTIONAL THEORY IN PRACTICE

Most of what has been described so far concerning density theory applies in theory rather than in practice. The fact that the Thomas–Fermi method is capable of yielding a universal solution for all atoms in the periodic table is a potentially attractive feature but is generally not realized in practice. Because of various technical difficulties, the attempts to implement the ideas originally due to Thomas and Fermi have not quite materialized. This has meant a return to the need to solve a number of equations separately for each individual atom as one does in the Hartree–Fock method and other ab initio methods using atomic orbitals. In addition most of the more tractable approaches in density functional theory also involve a return to the use of atomic orbitals in carrying out quantum mechanical calculations since there is no known means of directly obtaining the functional that captures electron density exactly.[20] Researchers therefore fall back on using basis sets of atomic orbitals which means that conceptually we are back to square one and that the promise of density functional methods to work with observable electron density has not materialized.

To make matters worse, the use of a uniform gas model for electron density does not enable one to carry out accurate calculations. Instead, 'ripples' or a density gradient, to use the more technical term, must be introduced into the uniform electron gas distribution. The way in which this has been implemented has typically been in a semi-empirical manner by working backwards from the known results on a particular atom, usually the helium atom (Gill, 1998). In this way it has been possible to obtain an approximate set of functions which often give successful approximate calculations in many other atoms and molecules. There is no known way of yet calculating, in an ab initio manner, the required degree of density gradient that must be introduced into the calculations.

By carrying out this combination of semi-empirical procedures and retreating from the pure Thomas–Fermi notion of a uniform

electron gas it has actually been possible to obtain computationally *better* results in many cases of interest than with conventional ab initio methods. True enough, calculations have become increasingly accurate but if one examines them more closely one realizes that they include considerable semi-empirical elements at various levels. From the purist philosophical point of view this means that not everything is being explained from first principles.

As time has progressed the best of both approaches (DFT and ab initio orbital methods) have been blended together with the result that many computations are now performed by a careful mixture of wavefunction and density approaches within the same computations (Hehre, 1986). This feature brings with it advantages as well as disadvantages. The unfortunate fact is that, as yet, there is really no such thing as a pure density functional method for performing calculations and so the philosophical appeal of a universal solution for all the atoms based on electron density rather than ficticious orbitals has not yet borne fruit.[21]

15. CONCLUSION

My aim has not been one of trying to decide whether or not the periodic system is explained *tout court* by quantum mechanics. Of course broadly speaking quantum mechanics does provide an excellent explanation and certainly one better than was available using only classical mechanics. But the situation is more subtle.

Whereas most chemists and educators seem to believe that all is well, I think that there is some benefit in pursuing the question of how much is strictly explained from the theory. After all, it is hardly surprising that quantum mechanics cannot yet fully *deduce* the details of the periodic table that gathers together a host of empirical data from a level far removed from the microscopic world of quantum mechanics. As Roald Hoffmann's title at this memorial meeting stated, "Most of what's interesting in chemistry is not reducible to physics" It is indeed something of a miracle that quantum mechanics explains the periodic table to the extent that it does at present. But we should not let this fact seduce us into believing that it is a complete explanation. One thing that is clear is that the attempt to explain the details of the periodic table

continues to challenge the ingenuity of quantum physicists and quantum chemists. For example, a number of physicists are trying to explain the periodic table by recourse to group theoretical symmetries in combination with quantum mechanics (Ostrovsky, 2000). Meanwhile the theoretical chemist Herschbach and colleagues have worked on a number of approaches which also aim at obtaining a global solution to the energies of the atoms in the periodic table (Kais et al., 1994)

Perhaps philosophers of chemistry have a role to play here. Unconstrained by what can presently be achieved, or even what might be achieved in the foreseeable future, one can point out the limitations of the current state of the art and one can place the research in the wider context of scientific reductionism in general and what it might mean for a calculation to be really ab initio. This is not a denial of the progress achieved in quantum chemistry or a reproach of the current work. It is more of an unrestrained look at what more could conceivably be done. Of course this might require a deeper theory than quantum mechanics or maybe a cleverer use of the existing theory. There is really no way of telling in advance.

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I would like to thank John Bloor for his highly incisive comments on many aspects of the work discussed in this article. Nevertheless I am sure he will not agree with all that I write here. I also thank Roald Hoffmann and other participants at the Rosenfeld memorial meeting for making some interesting comments from which I have greatly benefited.

NOTES

[1] Another way of regarding the same question is to consider typical 'chemical explanations', full of visualizations and sometimes naïve realism, and contrast them with the more abstract mathematical explanations favored by the physicist.

[2] In fact the fourth quantum number does not emerge from solving Schrodinger's equation. It was initially introduced for experimental resons by Pauli, as a fourth degree of freedom possessed by each electron. In the later treatment by Dirac the fourth quantum number emerges in a natural manner.

[3] The fourth quantum number does not emerge from solving the Schrödinger equation.

[4] It is gratifying to see that this article has now been cited by about twelve chemistry textbooks including those by Atkins, Huheey, Levine etc.

[5] It should be noted that the Hartree–Fock method uses four quantum numbers which are given the same labels as those in the hydrogen atom. However these are not identical but only analogous. This fact is often overlooked in elementary presentations which imply that the two sets are identical.

In a recent paper Ostrovsky has criticized my claiming that electrons cannot strictly have quantum numbers assigned to them in a many-electron system (Ostrovsky, 2001). His point is that the Hartree–Fock procedure assigns all the quantum numbers to all the electrons because of the permutation procedure. However this procedure still fails to overcome the basic fact that quantum numbers for individual electrons such as l in a many-electron system fail to commute with the Hamiltonian of the system. As a result the assignment is approximate. In reality only the atom as a whole has quantum numbers, not individual electrons.

[6] Charlotte Froese Fischer was a PhD student of Hartree's in Cambridge and pioneered accurate calculations using the method initially devised by Hartree.

[7] Admittedly Hartree–Fock calculations whether relativistic or not omit correlation effects in atoms since they involve time averages of electron repulsions.

[8] Broadly speaking it is still an orbital based method of course but not one that corresponds to the elementary concept of a particular number of electrons in the shells of an atom.

[9] In fact given that the C.I. approach involves a mixture of so many different configurations it is capable of calculating the energy of the entire atom but not specifically of the ground state configuration.

[10] The CISD method produces typical errors of 0.4–0.7 eV for the ground states of elements from manganese to copper even after the inclusion of relativistic effects. The Coupled Cluster method called CPF produces an error of 0.4 eV for the d^8s^2 to d^9s^1 splitting in nickel. The basis set cited in the main text comes from a study in which an elaborate quadratic CI method was used in which the already large basis set was augmented with numerous 'diffuse' orbitals (Raghavachari and Trucks, 1989). The use of M-P perturbation theory produced what the authors of this article describe as "wild oscillations" for the same excitation energy.

[11] I am doing a certain amount of back-tracking given that this method was mentioned above when some results were quoted for transition metals.

[12] In fact there are some other good reasons to support the placement of helium in the alkaline earths, contrary to popular opinion among chemists as I will be exploring in a forthcoming article.

[13] Although as noted the configuration of Ni is actually $4s^13d^9$ contrary to what is stated in most textbooks.

[14] The question for realism is altogether different if taken in the sense of the belief in unobservable scientific entities. In fact many philosophers of science currently favor some form of scientific realism in the context of quantum mechanics (Cao, 2003).

[15] So I advocate realism about chemical reactions that can be observed macroscopically without being a realist about electrons in shells.

[16] But Teller showed that the Thomas–Fermi model cannot predict binding in atoms.

[17] This is why I and some others have been agitating about the recent reports, starting in Nature magazine in September 1999, that atomic orbitals had been directly observed. This is simply impossible (Scerri, 2000).

[18] I have tried to stress the educational implications of the claims for the observation of orbitals in other articles and will not dwell on the issue here (Scerri, 2000, both articles cited for that year).

[19] Of course it is a matter of taste whether one uses ficticious orbitals or real and observable electron density.

[20] Promise due to theorems proved by Hohenberg and Sham and Kohn.

[21] Some preliminary work aimed at developing pure density methods has been carried out (Wang and Carter, 2000).

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CORRIGENDUM

E.R. Scerri. Just How Ab Initio is Ab Initio Quantum Chemistry? *Foundations of Chemistry* 6: 93–116, 2004.

p. 99. The configurations for Cu and Zn shown in Table I are incorrect. They should read:

Cu $4s^1 3d^{10}$ Zn $4s^2 3d^{10}$

p. 107. The configurations for Pd and Pt are incorrect and should read:

Pd [Kr] $5s^0 4d^{10}$

Pt [Xe] $6s^1 5d^9$

Some Aspects of the Metaphysics of Chemistry and the Nature of the Elements

Eric R. Scerri

Abstract: There is now a considerable body of published work on the epistemology of modern chemistry, especially with regard to the nature of quantum chemistry. In addition, the question of the metaphysical underpinnings of chemistry has received a good deal of attention. The present article concentrates on metaphysical considerations including the question of whether elements and groups of elements are natural kinds. It is also argued that an appeal to the metaphysical nature of elements can help clarify the re-emerging controversies among chemists regarding the placement of the elements hydrogen and helium in the periodic system and the question of whether there exists a best form of the periodic table.

Keywords: *Metaphysics, element, periodic table, reference theory, Kripke & Putnam.*

1. Introduction

A good deal of work carried out up to this point has been of an epistemological nature, such as the examination of the reduction of chemistry to quantum mechanics by a number of authors (*e.g.* Ramsey 1997, Needham 2000, Woody 2000, Scerri 2001). However, given the recent growth in the study of the philosophy of chemistry, it seems appropriate to consider also the metaphysical aspects of the field.

In the philosophy of physics, metaphysical considerations have been examined for some time and they continue to be the focus of much attention. For example Cao has devoted a great deal of effort in arguing that a metaphysical understanding of quantum field theory is essential in trying to comprehend the nature of quantum mechanics. While Cao argues for a physical ontology consisting of entities, others equally interested in the metaphysical foundations of physics argue that the ontology lies not in particles or entities but in the mathematical structure of quantum field theory (Cao 2003, French & Ladyman 2003). In the philosophy of biology one of the topics of interest

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has been the question of whether biological species are natural kinds or not (Ghiselin 1974, Hull 1977, LaPorte 2004). Several authors have appealed to the metaphysical foundations of biology in order to clarify such questions (Hull 1977).

In chemistry the prospects for a metaphysical project might appear to be gloomy at first sight. Whereas theoretical physics has been increasingly forced to embrace an abstract ontology that focuses attention on the vacuum fluctuations, a similar move has not occurred in chemistry. Chemistry generally speaking stops at non-relativistic or relativistic quantum mechanics and does not generally require the use of a full-blown quantum field approach and an appeal to the quantum mechanical vacuum.[1]

In addition, the appeal to metaphysical considerations appears to be undermined because many commentators have falsely claimed that chemistry has become a reduced science or a service science to physics and biology (Knight 1992, pp. 157-170; Bensaude-Vincent & Stengers 1996, pp. 207-252). Indeed chemistry is regarded as an increasingly utilitarian science by many chemists themselves. The commonly held view that chemistry reduces to quantum mechanics would seem to obviate a need for a specifically chemical ontology or metaphysics. But now that these reductionist claims have been increasingly challenged in the philosophy of science, this would seem to clear the way for more work on the metaphysics of chemistry.

Various philosophers of chemistry have already examined metaphysical aspects of chemistry and in particular the question of the elements as natural kinds (Schummer 1996, Bensaude-Vincent 1998, van Brakel 2000, Cahn 2002, Harré 2005, Lombardi & LaBarca 2005).

The present article will appeal to two interrelated metaphysical views concerning the chemical elements. The first such view is what may be called metaphysical in the naïve, or literal, sense of the elements as being beyond observation. The second metaphysical view considers the elements as the fundamental entities or natural kinds of chemistry. More work has been carried out regarding the latter, including the question of whether the elements actually represent natural kinds. For example, the Kripke-Putnam causal theory of reference has led to a good deal of discussion of precisely how elements should be referred to and the question of their essential properties. There are some interesting connections between these two metaphysical aspects of the elements, that will be indicated as the article proceeds.

2. First sense of metaphysics: Elements as unobservable substances

A long-standing metaphysical view about the nature of elements has regarded them as basic substances or as bearers of properties. This view has never been completely abandoned in chemistry and I will argue that it can be brought up to date to serve our present needs. The chemical elements, in the unobservable sense, were first invoked by some Greek philosophers and continued to play a role up to the beginning of 20th century chemistry, although in a modified sense.

The manner in which philosophically inclined chemists have regarded elements is concerned with the ancient question of how the elements survive, if at all, when they form compounds. This conundrum has been classically resolved, since the time of the ancient Greek philosophers, by appealing to the dual sense of the term 'element'. An element can be regarded as a 'simple substance' that can be isolated and that can take several different structural forms, such as diamond or graphite, in the case of carbon. In addition, an element can also be regarded, more fundamentally, as a 'basic substance', which is the bearer of properties while at the same time being devoid of properties.[2] This metaphysical view, in the sense of elements as unobservable bearers of properties was partly abandoned as a result of the chemical revolution. Lavoisier found it more useful to concentrate on elements as observable simple substances that can be isolated. As many authors have argued, Lavoisier did not succeed in completely banishing the notion of elements as unobservable bearers of properties, but this question will not be pursued any further here (Siegfried 2002).

It appears that the notion of elements as basic substances made its comeback in the writing of Mendeleev who insisted that his periodic classification was primarily concerned with this sense of the term 'element' and not as observable simple substances. However, Mendeleev did not merely return to the ancient view whereby the elements as basic substances were completely devoid of properties or characteristics. For Mendeleev a basic substance possessed at least one attribute, namely its atomic weight which served to distinguish it from other elements and which was used to order the elements in a unique sequence.

The distinction between elements as basic substances and as simple substances was held to be of crucial importance by Mendeleev. There are many passages in his classic textbook, *The Principles of Chemistry*, in which he goes to great lengths to explain it.

> It is useful in this sense to make a clear distinction between the conception of an element as a *separate* homogeneous substance, and as a *material* but invisible *part* of a compound. Mercury oxide does not contain two simple bodies, a gas

> and a metal, but two elements, mercury and oxygen, which, when free, are a gas and a metal. Neither mercury as a metal nor oxygen as a gas is contained in mercury oxide; it only contains the substance of the elements, just as steam only contains the substance of ice, but not ice itself, or as corn contains the substance of the seed but not the seed itself. [Mendeleev 1891, p. 23]

In the 20th century Paneth, one of the founders of radiochemistry, similarly upheld the view that it is only the element in the second sense, as a basic substance, that survives when sodium and chlorine combine to create sodium chloride. On the other hand, sodium and chlorine, as simple substances, consist of a gray metal and a green gas respectively, properties that do not survive when these elements combine together as simple substances. However, drawing on the recent discoveries of physics and especially the work of Moseley, Paneth changed the characteristic of an element as a basic substance from its atomic weight to its atomic number (Paneth 1962).

In addition, Paneth's philosophical message was to suggest that chemists typically adopt an 'intermediate position' between what he termed naïve realism and a metaphysical view. At other times, Paneth described this contrast as being one between naïve realism and the reductive view provided by physics. Such distinctions may sound rather unusual to modern philosophers and, of course, Paneth was not a professional philosopher, thus possibly accounting for his choice of terminology. However, what Paneth had to say on the nature of chemistry and the elements, coupled with the fact that he was responsible for the introduction of the current definition of a chemical element, obliges us to examine his philosophical views more closely. One might consider that Paneth's terminology is somewhat unfortunate since he was not contrasting realism in general with metaphysics as these positions are generally understood, nor was he contrasting realism with reductionism as generally understood. Instead, Paneth was contrasting a macroscopic view of chemical phenomena (naïve realism) with a microscopic description (reduction to physics). But it must also be appreciated that Paneth's view was centered on the contrast between elements as simple substances (naïve realism) and elements as basic substances (metaphysical in the sense of being beyond observation). For Paneth reduction via physics represented a process leading to less and less observability of the kind that is more familiar to the chemist.[3]

Paneth claimed that the chemist could afford to take a naïvely realistic attitude in the case of most observed properties. For example, the ore of mercury, called cinnabar, can be regarded as just being red even though the chemist knows that the red color can be further reduced to a specific range of frequencies of reflected light. But Paneth also claimed that such a form of naïve realism, as accepting elemental properties at face value, breaks down when the chemist is confronted with the question discussed earlier regarding the persistence of elements in compounds. In such a case, the chemist is

forced to abandon the naive realistic view of elements as simple substances, and must maintain what he termed a metaphysical view[4], in the sense of elements as unobservable basic substances. Paneth suggested that chemists generally operate at an intermediate position, which is neither fully naïvely realistic nor metaphysical, in his terminology. I suggest that, in spite of such terminological pitfalls, Paneth's view is philosophically consistent.[5]

It is proposed that Paneth's view of the elements might serve to illuminate a number of issues in contemporary philosophy of science as well as in chemistry. But before doing so it is important to summarize the changing view of elements as basic substance from that of the ancient Greeks through Mendeleev's and Paneth's views. For some Greeks philosophers the elements as basic substances were completely unobservable. For Mendeleev elements as basic substances remained "invisible" to cite his own word, but were characterized by one main property, namely atomic weight. It would appear that the elements as basic substances had lost their fully metaphysical characteristic of being completely unobservable, and devoid of properties, since they now possessed one important attribute. Similarly, Paneth's understanding of elements as basic substances did not imply complete unobservability and was not a thoroughgoing metaphysical view in the literal sense mentioned earlier. For Paneth elements as basic substances possessed one important attribute, namely atomic number.[6]

3. Second sense of metaphysics: Elements as the basic entities of chemistry or its natural kinds

The beginning of this section may be familiar territory to analytical philosophers but perhaps not so to a chemical audience. A brief historical sketch of the developments in this area will therefore be given.

The motivation for the causal theory of reference and its criteria for referring to natural kinds has been a central question of how language relates to the world. Traditionally, expressions such as proper names refer to or designate an object because the name was associated with some descriptive content about the object in question. Analogously, general terms or nouns such as 'tiger', 'acorn', or 'element' were considered to refer to objects by virtue of their 'sense' where the sense provides the description of the object (Frege 1892).

This conception of the relationship between language and reality came under criticism in the 1960s and 1970s from a number of philosophers (Donnellan 1966, Kripke 1972, Putnam 1975). The gist of this criticism was that a description associated with a name or term like 'tiger' did not provide necessary and sufficient conditions for its application to the object in question.

For example, a speaker might be referring to a tiger although the creature in question did not have the familiar stripes, in the case of an albino tiger. Conversely, an anomalously colored creature might display the striped appearance of a tiger while belonging to an altogether different species.

Or one might consider an example from Kripke involving the proper name 'Aristotle'. According to the traditional theory of names, at least some of the descriptive concepts usually believed of Aristotle are regarded as being necessarily true of the famous philosopher. However, as Kripke points out, it would be odd to regard it as necessarily true that Aristotle was a teacher of Alexander, or the pupil of Plato, or that he was even a philosopher. Aristotle might not have actually played any of these roles had the course of history been different, claims Kripke. It was not essential for Aristotle that he should have engaged in any of these activities. In Kripke's terminology, the name 'Aristotle' refers rigidly to that man independently of any description associated with the name Aristotle. Similarly, Kripke believes that nouns like proper names are rigid designators. If 'gold' is such a rigid designator, it refers to the same stuff, independently of its superficial (descriptive) appearance. For Kripke 'gold' rigidly designates the element with atomic number 79.[7] It is not the description of gold in terms of being shiny or malleable *etc.* that determines whether some substance is gold but only its atomic number. Iron pyrite, as Kripke points out, is not gold because it does not possess an atomic number of 79, regardless of whether its appearance might resemble that of gold.

Intuitions of this kind led some philosophers to require that facts about the world should be regarded as matters of objective causal relations in the world and not ideas that people have in their heads. In this context, the Kripke-Putnam causal theory of reference was born. It was now claimed that nouns that are meant to designate natural kind terms do not have their extension determined by descriptive concepts but by a causal chain beginning with the original baptism or naming of a sample object. In addition, the reference of the term is provided by whatever is dictated by the latest scientific research, hence the use of atomic number in the case of any particular element. This last feature led Kripke and Putnam to adopt Paneth's definition of elements in terms of atomic number, since this remains as the most up-to-date scientific definition of an element.

4. Convergence of views?

If we now consider how an element is specified in chemistry and in the theory of causal reference, we reach an interesting situation. In chemistry, as

emphasized above, the understanding of the term 'element' was provided by Mendeleev, and later modified by Paneth, eventually leading to the definition of an element adopted by the International Union of Pure and Applied Chemistry. Elements are regarded as basic substances that are devoid of properties apart from having an atomic number which in any case is not macroscopically observable. Similarly, and for quite other reasons, Kripke and Putnam, approaching the issue with a different set of concerns, arrived at the conclusion that names of elements like 'gold' did not identify such samples by virtue of their descriptive content or 'properties'. They claimed that names connect with the world through one single criterion provided by modern chemistry, namely atomic number accompanied by a causal chain from the initial act of baptism.

The fact that the criterion for elementhood turned out to be the same, namely atomic number, is not so remarkable since the philosophers made a direct appeal to the scientific understanding of an element and therefore inherited atomic number straightforwardly. What is perhaps worth dwelling upon is the fact that both the chemical and philosophical understanding of an element involve a denial of its observable or descriptive attributes. In Paneth's chemical account an element, regarded as a basic substance, does not possess observable properties.[8] In the case of Kripke and Putnam the descriptive properties are commonly believed to exist but are ignored when referring to the element. I suggest that that there is convergence between Paneth and the philosophers Kripke and Putnam, and that both parties are dealing with the elements as basic substances and that important aspect of the causal theory of reference amounts to a denial of descriptive aspects. As far as I am aware this feature has not been previously noticed.

I suggest that the two apparently different metaphysical senses of the term 'element', namely an element as an unobservable basic substance and an element as a natural kind, may actually converge in the final analysis.

5. Putting elements as basic substances to work

In the 1920s Paneth drew on the metaphysical essence of elements as basic substances in order to save the periodic system from a major crisis. Over a short period of time many new isotopes of the elements had been discovered, such that the number of 'atoms' or most fundamental units suddenly seemed to have multiplied. The question was whether the periodic system should continue to accommodate the traditionally regarded atoms of each element or whether it should be restructured to accommodate the more elementary isotopes that might now be taken to constitute the true 'atoms'. Paneth's

response was that the periodic system should continue as it had done before, in that it should accommodate the traditional chemical atoms and not the individual isotopes of the elements.[9] The reason why Paneth regarded isotopes as simple substances is that they were characterized by their atomic weights and, as it will be recalled, basic substances were characterized by atomic number alone in Paneth's scheme.[10]

Moreover, Paneth along with Hevesy provided experimental evidence in support of this choice for chemists.[11] They showed that the chemical properties of isotopes of the same element were for all intents and purposes identical.[12] As a result the chemist could regard the isotopes of any element as being the same simple substance even though such atoms might occur in different isotopic forms.

It is worth noting that in the case of this isotope controversy, Paneth's recommendation for the retention of the chemist's periodic table depended on the notion of elements as basic substances and not as simple substances. If chemists had focused on simple substances, they would have been forced to recognize the new 'elements' in the form of isotopes that were being discovered in rapid succession. By choosing to ignore these 'elements' in favor of the elements as basic substances, chemists could continue to uphold that the fundamental units of chemistry, or its natural kinds, remained as those entities that occupied a single place in the periodic system. This represents a parallel case to that of the persistence of the elements in compounds, a situation in which chemists must likewise abandon naïve realism in favor of what Paneth called the metaphysical view of elements in order to rationalize the situation.[13]

6. Groups of elements as natural kinds?

Having argued, with Kripke and Putnam, that elements as defined by their atomic numbers represent natural kinds in chemistry, the question arises as to whether groups of elements appearing in the periodic table might also represent natural kinds. Could it be that there is some objective feature that connects all the elements that share membership to a particular group in the periodic system?

It would seem that the criterion for membership to a group is by no means as clear-cut as that which distinguishes one element from another. In the case of groups of the periodic table, it is the electronic configuration of gas phase atoms that seems to provide the criterion, although in neither a necessary nor a sufficient manner as has been argued in previous publications (Scerri 2004). However, one may also argue that the placement of the ele-

ments into groups is not a matter of convention. If periodic relationships are indeed objective properties, as will be argued here, it would seem to suggest that there is one ideal periodic classification, regardless of whether or not this may have been discovered. This in turn would have a bearing on some recent questions regarding the placement of some elements within the periodic system. And if electronic configurations do not perfectly capture the fact that groups are natural kinds, this may merely indicate the limitations of the concept of electronic configurations.[14]

7. The placement of H and He in the periodic system

There has been considerable debate within chemistry in recent years as to the placement of the elements hydrogen and helium within the periodic system (Cronyn 2003). For example, hydrogen is similar to the alkali metals in its ability to form single positive ions. However, hydrogen can also form single negative ions, thus suggesting that the element might be placed among the halogens that display this type of ion formation.

In a recent article, Peter Atkins and Herb Kaesz have proposed a modification to the periodic table concerning the placement of the element hydrogen (Atkins & Kaesz 2003). Contrary to its usual placement at the top of the alkali metals, and its occasional placement among the halogens, Atkins and Kaesz choose to position hydrogen on its own and floating above the table. In doing so these authors appear to overlook the further possibility of hydrogen's membership of the group that is usually headed by carbon, as has recently been argued in detail (Cronyn 2003).

But rather than considering the relative virtues of these three possible placements, let us consider the argument for the removal of hydrogen from the main body of the table a little more closely and from the perspective of the elements as basic substances. The widely held belief, among chemists, is that the periodic system is a classification of the elements as simple substances that can be isolated and whose properties can be examined experimentally. However, as I have emphasized, there is a long-standing metaphysical tradition of also regarding the elements as unobservable basic substances.[15]

Our current inability to place hydrogen in the periodic table in an unambiguous manner should not lead us to exclude it from the periodic law altogether, as Atkins and Kaesz seem to imply in removing hydrogen from the main body of the table. Hydrogen is as subject to the periodic law as all the other elements. I maintain that there is a 'fact of the matter' as to the optimum placement of hydrogen in the main body of the table and that this is

not a matter of utility or convention that can be legislated as these and other authors have argued. That is to say groups of elements should be regarded, as should elements themselves, as natural kinds as suggested above.

Helium is traditionally regarded as a noble gas in view of its extreme inertness and is subsequently placed among the other inert gases in group VIII of the periodic system. However, in terms of its electronic configuration helium has just two outer electrons and might therefore be placed among the alkaline earth metals such as magnesium and calcium. Many periodic tables appearing in physics books do just that, as do many spectroscopic periodic systems (White 1934).

Surprising as it may seem, some chemists have even proposed chemical evidence for placing helium in this manner. Such arguments are based on the first-element rule which, in its simplest form, states that the first element in any group of the periodic system tends to show several anomalies when compared with successive members of its group. For example, in the p block, all the first-member elements show a reluctance to expand their octets of outer-shell electrons, while subsequent group members do so quite readily.[16]

In addition, there is a more sophisticated version of this first-member rule that also specifies the extent to which the first elements in the various blocks of the Periodic Table display anomalies. For example, Jensen writes,

> It is also sometimes argued that H is placed above the table because it is totally unique in its properties. While it is true that H is unique relative to other IA elements, this is really a reflection of the systematic variation in the periodic table which shows that the elements in the later row of any new electronic block tend to show abnormalities relative to the elements in later rows of the same block, and that the degree of divergence decreases in the order s-block >> p-block > d-block > f-block. [Jensen 1986].

Another chemist, Bent, has taken up the sophisticated first-element rule, sometimes claiming it to be the same as Jensen's. According to Bent, "A group's first member is the group's most distinctive member, the more so the narrowest the group's block".[17] Bent considers the sophisticated first-element rule as an argument for the placement of helium in the s block. He believes that it is only by placing hydrogen and helium in the alkali metals and alkaline earths, respectively, that they fall into narrowest block in the Periodic Table. Bent believes that one would fail to see any manifestation of the sophisticated first-element rule, if one were to leave helium in the p block, as is done traditionally. However, the use of the first-member rule has also led to much disagreement among chemists. For example, Jensen, who was cited earlier, regards the rule as an argument *against* the placement of helium among the alkaline earths (Jensen 1986).

Rather than relying on specific properties of the elements as simple substances, it is suggested that we should concentrate on elements as basic sub-

stances. One should seek some form of underlying regularity in order to settle the question of the placement of any element. Such a possibility is discussed in the next section, along with the question of the best possible form for the periodic system.

8. Is there a best form for the Periodic Table?

The periods in the currently most popular representation of the periodic system, the so-called medium-long form, are arranged so that each one begins with a new value of n, or the first quantum number (Figure 1). This value denotes the main shell of the most energetic electron in each case, in terms of the aufbau principle, that is used to 'build-up' the configuration of any particular atom. In macroscopic chemical terms, the medium-long form table places the reactive metals, such as the alkalis and alkaline earths, on the left side of the Periodic Table and the reactive non-metals on the right side.

The conventional medium-long form displays the periods as though the main-shell number were the dominant criterion for the build up of successive periods. However, as is well known, this form of display leads to a somewhat confusing layout whereby in several cases a main shell begins to fill, followed by an interruption due to a transition metal series in which a penultimate shell is filled. Only after such interruptions, which are more pronounced in the case of periods that also include inner transition elements, does the filling of the main shell resume.

Many authors have suggested that a more satisfactory representation can be obtained by basing the start of periods on $n+l$ instead of n.[18] This implies that the s block must be shifted to the right of the p block elements, which leads more specifically to at least two particular Periodic Tables. The first one is the so-called left-step periodic table (Figure 2). The second is a *modified* form of the pyramidal periodic system that likewise places the s block elements on the right hand edge of a pyramid (Figure 3). Both of these tables display two short periods of two elements thus satisfying the desire for regularity that many authors, including some group theorists, believe might lie at the heart of the periodic system (Neubert 1970).

Both of these alternative representations of the periodic system shown in Figures 2 and 3 display the elements in a continuous manner with no break between any sets of elements, contrary to what is encountered in the currently accepted medium-long form. But these tables also contain a feature that causes many chemists some concern, in that the element helium is firmly located among the alkaline earth elements.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	

Figure 1: Medium-long form of the Periodic Table.

													H	He				1
													Li	Be				2
											B	C	N	O	F	Ne	Na	Mg	3
											Al	Si	P	S	Cl	Ar	K	Ca	4
				Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	5
				Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	6
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	7
Ac	Th	Pa	U	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg										8

Figure 2: The left-step or Janet Periodic Table; numbers on the right represent values of $n+l$.

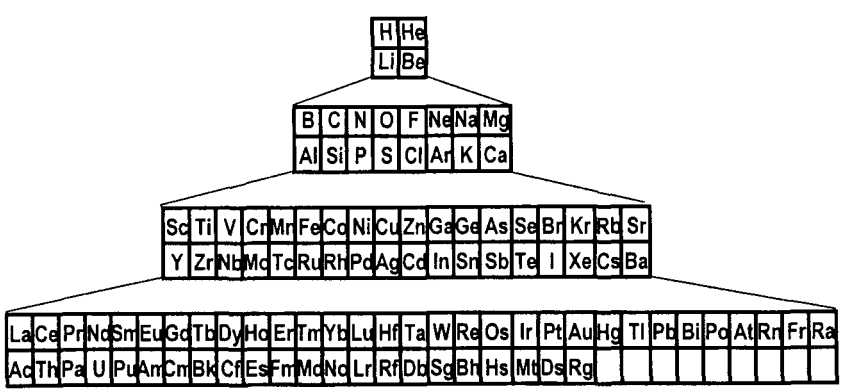
H He
Li Be
B C N O F Ne Na Mg
Al Si P S Cl Ar K Ca
Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Rb Sr
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe Cs Ba
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn Fr Ra
Ac Th Pa U Pu Am Cm Bk Cf Es Fm Md No Lr Rf Db Sg Bh Hs Mt Ds Rg

Figure 3: A modified pyramidal version of the Periodic Table.

However, as I have argued in the previous section, such worries are alleviated once one acknowledges that the periodic system is primarily intended to classify the elements as basic substances and not simple substances.

Moreover, I claim that there is a fact of the matter concerning the best form of the periodic system in the sense that all elements belong in a particular group. Periodicity applies to all the elements, or in philosophical terms, to groups of elements which represent natural kinds. I do not agree with some chemists who consider the representation of the periodic system as a matter of convention as exemplified by the quotations below. In the preface of his well-known book that compiles the various forms of the periodic system produced up to the year 1970, Edward Mazurs writes (1974, p. xi),

> The third section, the main part of the book, is based on a survey and analysis of the approximately seven hundred periodic tables published during the past one hundred years. The number and variety of these charts represent the ability of the human mind to give disparate forms to the same body of matter.

Similarly, in a recent article on a new presentation of the periodic system, the author writes (Stewart 2004, p. 156),

> Of the making of Periodic Tables there is no end. No version can ever be definitive because there are various incompatible objectives. Some authors provide a schematic version that is readable and easily reproduced, while others exploit devices such as the third dimension to express complexity. Some aim at simplicity or grace while others want to convey detailed information on such things as relative atomic mass, valency, electronic structure, melting and boiling points, electronegativity, radioactivity, metallic or non-metallic nature, geological affinities and so on.

The chemist Henry Bent (2004, p. 7) writes,

> One might wonder – which periodic table is best? As impossible as unnecessary to say? Best for what purpose(s)? Location of the problem elements? The left-Step Table. Discussion of horizontal trends in metal/non-metal character? The Left-step Table. Discussion of the most familiar elements, with beginning students? The Conventional [medium-long form] table [...] Graphic display of secondary kinships? Neither table. Better is Mendeleev's "Short Form".

Although one can partly agree with the view that different representations can help to convey different forms of information, I believe that one may still maintain that one particular representation reflects chemical periodicity, regarded as an objective fact, in the best possible manner. I am thus suggesting a realist view of the periodic law that requires believing that groups of elements, as well as elements themselves, are natural kinds.

9. Conclusions

The metaphysical notion (unobservable sense) of the elements as basic substances has been historically important in the case of Mendeleev's establishment of the periodic system and Paneth's resolution of the fate of the periodic system in light of the discovery of isotopes. A seemingly different metaphysical notion of elements in which they are regarded as natural kinds has been developed in philosophy in response to concerns about the manner in which names and scientific terms refer to objects in the world. It has been suggested in the present article that the two approaches may converge, thus implying that elements as basic substances are being invoked in the domains of chemistry as well as philosophy when discussing the elements.

It has also been suggested that the notion of elements as basic substances can cast some light on the question of the best possible representation of the periodic system. As in the case of the distinction between elements as basic substances and as simple substances, the primary aim should be to classify elements as basic substances, while also recognizing aspects of the elements as simple substances. This optimal classification will not be obtained by behaving as naïve inductivists and by agonizing over the minutiae of the properties of hydrogen, helium, or other problematic elements, as Jensen seems to favor (Jensen 2003). It is suggested that it will be obtained by identifying the deepest and most general principles that govern the atoms of the elements, such as the $n + l$ rule, and by basing the representation of the elements on such principles.[19]

Just as philosophically inclined chemists, like Mendeleev and Paneth, have resolved some major conceptual issues by appeal to the metaphysical nature of the elements, so can the contemporary philosopher of chemistry. Although all comments have thus far been restricted to the nature of the chemical elements, the appeal to a metaphysical approach should be promising in other areas of philosophy of chemistry, given the centrality of the elements in this field.

The above analysis is not intended to imply that the Kripke-Putnam theory of reference is free of any criticism. For example, two prominent philosophers of chemistry have objected to it on the basis that it relies too heavily upon micro-reduction. For example, van Brakel espouses a radical anti-reductionism in which he favors the 'manifest image' over micro-reduction. His writings have included a thoroughgoing critique of Kripke's and Putnam's theory and a review of all other critiques that have been made in the context of chemical kinds (van Brakel 2000). Similarly, Needham takes an anti-reductionist approach and prefers to define substances through the Gibbs phase rule (Needham 2005).

In addition some mainstream philosophers of science have pointed out the so-called *qua*-problem that has become to be viewed as increasingly problematic for the Kripke-Putnam account of reference (Devitt & Sterelny 1978, Stanford & Kitcher 2000). According to the Kripke-Putnam view, the scientific term 'gold', for example, involves ostentation of samples of the substance gold that possess an atomic number of 79. However, it is not clear *qua* member of which kind such a sample of gold is being ostended. It could be as a metal, as a solid, as a shiny substance, or any number of possibilities other than possessing atomic number 79. The response from some philosophers has been to suppose that the Kripke-Putnam view needs to admit some relaxation of its semantic externalism (Stanford & Kitcher 2000).

More recently a philosopher of chemistry, Hendry, claims to have an approach which can counter the *qua*-problem but without any relaxation of Kripke and Putnam's externalism (Hendry 2005). Hendry believes that what matters when scientists are referring to elements, for example, is their intentions. Indeed, Hendry's main example consists of an analysis of the term 'element' as used by a number of famous chemists. Hendry claims that the sense of the term appears to change if one considers the writings of Boyle, Lavoisier, Mendeleev, and Paneth. But he also claims that if we consider what these chemists intended by the term in their work, rather than what they actually claimed they were doing, then we will discover that there has been a continuity of reference with regard to the term 'element'. As I see it, there are some serious problems with Hendry's account which will form the basis of a forthcoming article (Scerri, forthcoming). Nevertheless I agree with this author that there has been a continuity of reference but disagree with the manner in which Hendry has attempted to establish this notion.

In spite of all these apparent shortcomings with the Kripke-Putnam causal theory as they apply to the term 'element', it is not my present task to analyze these problems. The purpose of this article has been to draw parallels between two senses in which the elements may be regarded metaphysically. The purpose has been to also draw parallels between the Mendeleev-Paneth definition of an element as a basic substance on the one hand, and the Kripke-Putnam account of elements as natural kinds on the other hand, both of which approaches deny observable properties to the elements. Finally, the purpose has been to apply the concept of elements as basic substances, which is explicit in the chemical definition and perhaps implicit in the Kripke-Putnam theory of reference, to contemporary issues concerning the placement of certain elements in the periodic system. Of course the overall purpose has been to stimulate further discussion on these issues which lie at the foundations of chemistry.

Dedication

This article is dedicated to Fernando Dufour, a leading pioneer of the periodic system, on the occasion of his 80th birthday.

Notes

1 Exceptions to the lack of use of QFT in chemistry include the work on the origins of optical activity (Barron 1982).

2 This particular terminology is due to Paneth. Although this sense of the term 'element' may sound somewhat mysterious, it should be pointed out that it was essential to Mendeleev's ordering of the elements in the periodic system. For example, if he had restricted himself to the properties of simple substances, he might not have grouped together fluorine, chlorine, bromine, and iodine, which are respectively a yellow gas, a green gas, a brown liquid, and a violet-black solid. It is rather the compounds of these elements that show close similarities. Here the elements are present as basic substances.

3 This sense of naïve realism is sometimes explained in terms of 'Eddington's table'. As Eddington wrote, if we remain at the macroscopic level, a wooden table appears to be solid and impenetrable. But if we consider the view from the perspective of a reductive physics, we learn that the atoms that make up the table are mostly empty space, a view that appears difficult to reconcile with the solidity of the table.

4 Paneth also used the term 'transcendental elements' to denote the elements as basic substances, a term borrowed from the 19th century German philosopher von Hartmann (Paneth 1962).

5 The position might not have been so coherent if Paneth had been speaking of completely unobservable elements, as did some ancient and medieval philosophers.

6 Robin Hendry has argued that Paneth is incorrect in his use of the word 'metaphysical' since Paneth is only referring to 'more abstract' elements in contrast to the more concrete simple substances (Hendry 2005).

7 Although Kripke allows that it is an empirical hypothesis that gold is the element with atomic number of 79, he also claims that if this hypothesis is correct then 'gold' rigidly designates the element with this atomic number.

8 Apart from atomic number which is detectable, if not directly observable.

9 Another radiochemist, Kasimir Fajans, was Paneth's leading opponent in believing that the periodic system would not survive the discovery of isotopes.

10 A reviewer has suggested that if Paneth's opponent Fajans had been willing to accept the notion of elements as basic substances, he could equally well have regarded the isotopes as basic substances. Although this possibility would appear to be plausible on philosophical terms, it could not have been an option for Fajans because it would have implied a return to the notion of characterizing the elements in terms of atomic weight rather than atomic number. The use of atomic number, discovered by Moseley and championed in chemistry by Paneth, solves

the problem of pair reversals. For example, the elements tellurium and iodine fall in chemically incorrect places on the periodic table if they are ordered according to atomic weight. The use of atomic number justifies their reversal as was carried out by the pioneers of the periodic system. From this point on, elements were identified by their atomic numbers and not their weights. The discovery of isotopes that differ in terms of weights does not alter the fact that elements as basic substances were henceforth to be characterized by atomic numbers. Isotopes are examples of simple substances since they represent instances of the elements that can actually be isolated, by contrast with the abstract atom of any particular element that occupies a space in the periodic table.

[11] Paneth and Hevesy showed that the electrochemical potential from two cells made from different isotopes of the metal bismuth was the same as far as experimental techniques of the day could distinguish (Scerri 2000).

[12] The fact that more recent research has revealed some differences even in the chemical properties of isotopes does not alter the central issue under discussion.

[13] Paneth did not fully commit himself on the question of metaphysical elements. He merely stated that he is using the terminology developed by philosopher von Hartmann (Paneth 1962).

[14] Electronic configurations are known to be approximations, unlike atomic number which can be given a clear realistic interpretation in terms of the number of protons in the nucleus of any atom (Scerri 2004).

[15] Once again unobservable apart from their possessing an atomic number.

[16] For example, oxygen, a first member element, forms OF_2 with eight electrons in the outer shell of oxygen. However, sulfur the second member of the group readily forms SF_6 in which twelve electrons occur in the outer shell of the sulfur atom (octet expansion).

[17] Bent, in preparation; what Bent has actually written here is "the shorter the group's block". The word 'shorter' normally indicates the vertical dimension of a block which is not what the author intended. This error was later confirmed to me by the author via personal correspondence.

[18] Janet 1929, Simmons 1948, Sanderson 1964, Katz 2001. The l or second quantum number is related to the n quantum number. For any given value of n, the value of l can adopt any integral value from 0 up to and including the value n-1.

[19] As in the use of atomic number, the use of the $n+l$ rule appeals to elements as basic substances and not as simple substances. This rule represents a generalization concerning all the elements, although it is violated in some instances, and is not concerned with any directly observable properties of the elements.

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Section C

Realism and Anti-Realism, and Educational Issues in Philosophy of Chemistry

Constructivism, Relativism, and Chemical Education

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ABSTRACT: **Whereas most scientists are highly critical of constructivism and relativism in the context of scientific knowledge acquisition, the dominant school of chemical education researchers appears to support a variety of such positions. By reference to the views of Herron, Spencer, and Bodner, I claim that these authors are philosophically confused, and that they are presenting a damaging and anti-scientific message to other unsuspecting educators. Part of the problem, as I argue, is a failure to distinguish between pedagogical constructivism regarding students' understanding of science, and constructivism about the way that scientific knowledge is acquired by expert scientists.**

KEYWORDS: **constructivism; relativism; chemical education; Science Wars; realism**

INTRODUCTION

For some years, the academic world has been in the midst of a fierce debate that shows little sign of abating. I am referring to what is popularly knows as the Science Wars, which began following the publication of Gross and Levitt's book entitled "Higher Superstition."[1] The charge made by these authors was that many who have written on the nature of science are seriously mistaken and are having a damaging influence upon scholarly work, the public image of science, and last but not least, on science education.

Briefly put, defenders of the traditional understanding of science (such as Gross and Levitt) complain that some sociologists, anthropologists, literary critics, and others have supported relativistic views, which threaten to undermine the fabric of scientific knowledge. The opposing side, which includes many of those belonging to the discipline that calls itself Science Studies, has defended itself in equally strident terms, although not as convincingly, to my mind. Many of the members of this opposing faction support constructivist views about scientific knowledge and about the learning of science. They draw their inspiration from a variety of sources ranging from Thomas Kuhn, in history and philosophy of science, to Jean Piaget, in psychology. There is much variety regarding the meaning of terms such as "constructivism"

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among authors, and this has added to the general confusion among Science Wars adversaries and even allies.

More recently, the Science Wars reached something of a crescendo following the publication of Alan Sokal's article in the journal *Social Text*.[2] Sokal, a theoretical physicist who believes that the postmodern commentators on science are mistaken, wrote a paper in which he imitated the style of these scholars by drawing analogies between research in modern physics and mathematics. Sokal's article was accepted by the journal in question and promptly published. At the same time, the author revealed, in another journal, that the article had been a prank intended to expose the sloppiness of the review process among postmodern commentators on science. His prank seemed to show that complete nonsense could apparently be made to pass for scholarly work in these circles.[3] Not only did Sokal's ingenious mischief inflame passions within the already divided academic community, it also attracted the attention of lay readers. The fallout of the Sokal affair has been examined in many commentaries, editorials, and debates appearing in newspapers and public forums of various kinds.

WHAT ROLE FOR CHEMISTRY IN THE SCIENCE WARS?

It appears that, in keeping with the low profile they display in philosophy of science, chemists have been almost completely invisible in discussions on the Science Wars, with just a few exceptions.[4] But I would like to suggest that some chemical educators (I will cite a few below) are also actors in the unfolding drama, in a way that has not been generally acknowledged. In addition, I advance the more startling notion that, unwittingly, these chemical educators are fighting on the wrong side of the battle. If one looks closely at the philosophical positions offered by these chemical educators, one sees many radical themes that confirm that many of them have indeed defected to what the science lobby would regard as "the opposition."

As a recent article pointed out, there are now a number of U.S. institutions that award Ph.D.'s in chemical education research.[5] However, the field continues to be viewed by the majority of mainstream chemists with suspicion, and sometimes even with hostility. It is not uncommon to hear of junior tenure-track faculty who are under undue pressure to perform according to unrealistic criteria set by departments that do not understand, or value, the nature of research in chemical education. Indeed, one hears from some full professors, in the institutions that do have specialists in chemical education, that these are marginalized and misunderstood by their traditional chemical colleagues. It is frequently said that research in chemical education represents a soft option, suited for those who are not capable of succeeding in "real chemistry."

I believe that part of the blame for the current state of affairs lies, not with the majority of mainstream chemists, but with the field of chemical education itself. One has only to attend a chemical education session at an American Chemical Society meeting to see that the field has become somewhat inward looking and self-congratulatory. One of the biggest failings, as I see it, is a lack of engagement in issues of chemical content. Instead, chemical education research frequently withdraws into producing better visualizations, and developing multi-media projects, in the hope of improving the teaching of chemistry. Such innovations often leave the subject of

chemical content as a mysterious black box that is supposed to look after itself. Mainstream chemists understandably view such activities as superficial busywork.

In this article, my aim is to concentrate on another aspect of research in chemical education, one that I believe to be more harmful to the reputation of the field. I refer especially to some dubious and abstract theoretical issues revolving around the themes of constructivism, relativism, and other philosophical "-isms."

My focus in what follows will be on the work of some chemical educators who call themselves "constructivists." Of course, mere adherence to a constructivist perspective need not be taken to mean any form of radical constructivism, of a social or individual kind, such as that which has recently angered the scientific community. But if one looks closely at the philosophical positions offered by some contemporary chemical constructivists, one sees many radical themes that are not only open to serious question but can also be construed as being anti-scientific. In other cases, I will suggest that chemical educators who call themselves constructivists are unwittingly supporting a very traditional conception of scientific knowledge that sits rather uncomfortably with constructivism as generally understood. In the following cases, I will be more concerned with philosophical motivations and commitments, as far as these may be discerned, than with detailed chemical examples, although some of the latter will also be touched on.

ORIGINS OF CHEMICAL CONSTRUCTIVISM

In a much-cited article that is regarded as a manifesto for chemical constructivism, Dudley Herron drew on Piaget's stages of psychological development and especially the transition between concrete and formal thinking.[6] Herron has become the undisputed leader in the movement to further what I will term "chemical constructivism." He is widely quoted in this context by authors who then proceed to offer what they regard as experimental support for the use of constructivism in chemical education. From a philosophical perspective, this tendency seems rather inexplicable. I can only surmise that the term constructivism is being used in a quite different sense of psychological or pedagogical constructivism rather than the philosophical or social constructivism often associated with Thomas Kuhn and others. But presumably there should be a connection between these two different forms of constructivism since a society of scientists comprises a collection of psychological individuals. If constructivism operates at the social level it might presumably be due to its also operating at the individual level. Perhaps some of the confusion philosophers experience on hearing the views that are voiced in chemical constructivism, and science education generally, is due to the gap between these two levels, the psychological and the social.

But to return to Herron, I believe that he is at heart an empiricist and that he makes no secret of this fact in many of his writings. Why he or his followers should label such views with constructivism is something that I propose to explore a little in this article. Herron has argued, as did Piaget before him, that many high school and beginning college students may not have effected the transition to the stage of formal reasoning. Herron's response is that we should take account of this fact in the way in which chemical education is approached. For example, in discussing the

topic of acid-base chemistry, Herron adopts what seems to be an essentially empiricist stance.

> I have suggested that the concept of an acid as anything that will turn litmus red is a concrete concept. The meaning of the concept is easily apprehended from sensory observation and requires simple classification skills. But I have also suggested that the concept of an acid as anything that will produce hydrogen ions in water solution (Arrhenius), as a proton donor (Brønsted-Lowry) or as an electron-pair acceptor (Lewis) is formal. The meanings of acid cannot be made clear through the senses directly since there is no way to sense protons or electron pairs. Rather this concept of acid can have meaning only through imagination or through logical thought about the nature of molecules which interact.[7]

It appears that Herron is interpreting Piaget's sense of the concrete in a narrowly empiricist fashion. Clearly Herron regards only things that can be seen, or sensed directly, as being concrete.

But I think that Herron has introduced something of an inconsistency, since the kind of empiricism to which he appeals—namely, the demand that scientific knowledge should have its foundation in sense perception—stands in direct opposition to virtually all forms of constructivism. Constructivism instead upholds that scientific knowledge is not so much discovered but negotiated or "constructed" by social factors or in the mind of the scientist or the learner.

But in all fairness to Herron, a close inspection of his much-cited article, as well as a subsequent one entitled "Piaget for Chemists," reveals absolutely no reference to constructivism, either psychological or social. What these early articles show is that Herron advises chemical educators to make chemistry instruction more concrete, since so many students have apparently not reached the more formal or more abstract stage of reasoning. Herron does finally acknowledge that it might also be an idea to find ways of accelerating the student's entry into the formal level of operation.

> Chemistry, and most of science, is formal by its very nature. Recognizing this we cannot continue to duck our responsibility for the development of formal thought.[8]

But he immediately reverts to the concern shown in his entire paper, namely, the need to make chemical issues more concrete.

> There are some studies which show that education can lead to improvement in formal thinking. We are in the exploratory stage of research in this area but there are consistencies that seem to be emerging. First, the inclusion of concrete experience—i.e. opportunities to actually touch, smell, see, and manipulate materials that would lead to the concept—appears to be important.[9]

No attempt to connect these Paigetian views with any form of constructivism whatsoever has been conducted by Herron in any of his articles in the *Journal of Chemical Education*. Indeed, in all his publications in that journal, I don't believe he has used the word "constructivism" on a single occasion!

The first, and perhaps the only, article in that journal that has attempted to connect the work of Paiget and Herron with constructivism of a psychological kind is one written by George Bodner.[10] In this article, Bodner claims that constructivism is the accepted view among psychologists. Of course, this may be so. It is not for me to comment on this claim. But Bodner also makes a number of rather dismissive remarks on the subject of realism. These claims by Bodner show that there is indeed a gulf between psychological constructivism and philosophical constructivism, for the simple reason that constructivism is by no means the predominant view among phi-

losophers of science. In addition, far from being an abandoned position in philosophy of science, scientific realism continues to flourish, and indeed appears to be the predominant view—opposed only by van Fraassen and his supporters.[11] I also note that Herron himself gives a brief discussion of how his views are supposed to constitute a form of constructivism, but this discussion appeared in a book that was published only in 1995.

The appeal to a nonspecific "constructivism" in the chemical education literature is somewhat ambivalent and continues to cause confusion. The only attempt to express disagreement with full-blown philosophical constructivism that has been made by any chemical educator, that I am aware of, was made by Herron in his book on chemical education, in which he cites another author approvingly as saying

> [even] though in some "ultimate" sense there is no way to determine whether one paradigm is a better approximation to the "real" laws on nature than another, the exclusion of nature and the empirical world from our model of how scientific knowledge grows makes it difficult to understand why some knowledge enters the core and most does not. Thus it is on practical sociological grounds that I select my realist perspective.
>
> Nature poses some limits on what the content of a solution adopted by the scientific community can be. By leaving nature out, the social constructivists make it difficult to understand the way in which the external world and social processes interact in the development of scientific knowledge.[12]

Herron then adds that

> [if] we are to understand learning, the only viable position to take is that an external reality exists, even though the understanding of it may differ from one person to another and from one point in time to the next.[13]

Although this word of caution represents a welcome improvement on the writings of other chemical constructivists, it does not go nearly far enough in moderating radical constructivist claims. It addition, it fails to distinguish clearly between philosophical and pedagogical constructivism. The author unfortunately also adds a footnote to tell readers that they can safely skip this entire section since it deals with an "obtuse point." As I see it, this section is absolutely essential to anyone involved in chemical education that might be drawn to constructivism, and should be made required, rather than optional, reading.

It is also unfortunate that Herron's followers in chemical education research, some of whom have been cited in the present article, have not seen the need to specify the precise sense in which they are using such terms as constructivism and relativism. Bodner and colleagues in particular appear to support an unqualified form of relativism, as I argue below, and which I maintain is anti-scientific in spirit.

THE "BEFORE AND AFTER" TREATMENT

Meanwhile, another chemical constructivist gives what can only be described as a simplistic comparison between what he terms "objectivism" and "constructivism" (TABLE 1).[14] Unfortunately, this tendency to present constructivism as though it were a form of weight reduction treatment, complete with "before and after" snapshots, is only too common in chemical education research.

The first of the three statements in TABLE 1 is difficult to interpret as it stands, since the author does not feel the need to qualify what is intended any further. Given

TABLE 1. Distinctions between objectivism and constructivism proposed by Spencer, a chemical constructivist

Objectivism	Constructivism
Truths are independent of the context in which they are observed.	Knowledge is constructed.
Learner observes the order inherent in the world. Aim is to transmit knowledge experts have acquired.	Group work promotes the negotiation of and develops a mutually shared meaning of knowledge. Individual learner is important.
Exam questions have one correct answer.	The ability to answer with only one answer does not demonstrate student understanding.

the scope of the article, namely chemistry and chemical education, I can only presume that the author is referring to scientific truths. The claim appears to be that objectivity is a myth regarding scientific findings whereas, according to the entry in the right-hand column, knowledge of scientific facts is constructed rather than objectively discovered. Needless to say, there may be ways of arguing for the importance of the context of scientific discoveries. After all, the growth of the Science Studies movement attests to such interests among historians and philosophers, but to reduce any such argument to the form of a one-line statement can only be described as an irresponsible move. This is especially so since such articles are intended for consumption by chemical educators who are generally not familiar with the detailed arguments that have been presented in the historical and philosophical literature. It is from chemical education researchers that chemical educators obtain their philosophical education, since they do not generally have the time or inclination to engage with the primary literature in history and philosophy of science.

In fact, to adopt a somewhat naïve view, the statement that "truths are independent of the context in which they are observed" is essentially correct, contrary to what the author implies. Indeed, it is a central belief for anyone either practicing or teaching science. If one were to believe the contents of the TABLE 1, one might conclude that a scientific truth would differ according to whether it was obtained at different geographical locations or at different times of the year, which is patent nonsense.

Similarly, if the author does not give any further qualification, the statement that "knowledge is constructed" is either plainly incorrect or so uncontroversial as to be superfluous. If the author implies that human preference dictates whether the magnitude of the speed of light is either 3 or 6 or 9×10^8 m/sec, approximately, this is simply untrue. If, on the other hand, the author is referring to the fact that all scientific knowledge is devised by human beings rather than being given to us directly by Nature itself, then, of course everyone, even the most rabid "objectivist," would probably concur.

The third entry in TABLE 1 is also a gross oversimplification. Unless the author is prepared to qualify the statement that "exam questions have one answer," which he implies to be mistaken, I don't believe he is expressing any position whatsoever. If the exam question is something along the lines of "What is the velocity of light in a vacuum?" then even a radical constructivist would have to concede that there is only

one correct answer. One exception might be the possibility of quoting the velocity to varying degrees of accuracy, but this does not seem to be the kind of thing that the author intends. Indeed, in the particular case of the velocity of light, there is absolutely no possibility of there being more than one response to the question, given the peculiar nature of light.

Alternatively, if the author is thinking of an open-ended question, such as whether Bohr's theory resolved the question of the collapse of the Rutherford atom, then many might respond that there may be more than one answer. As in the previously considered case, one does not need to be a constructivist to accept the entries in the right-hand column under certain circumstances. But to claim that knowledge is constructed in general, or that the majority of exam questions have more than one answer is, I think, the height of folly.

It is not mature scientific knowledge that is constructed, but only the student's *understanding* of mature science, a theme that I return to below.

RELATIVISM WITH A VENGEANCE

One of the worst confusions set loose among chemical educators has been the notion of relativism. In an unpublished but widely distributed article, as well as a published one, George Bodner and colleagues leave the reader in no doubt about their own stance on this question.[15] Bodner and colleagues appear to have latched onto a rather idiosyncratic interpretation of relativism that they claim to support. This is what they write:

> The difference between the traditional and constructivist theories of knowledge mirrors the difference between the philosophy of science known as realist, objectivist, or positivist, and the philosophy of science known as relativist. ... Realists believe that logical analysis applied to objective observations can be used to discover the truth about the world in which we live. They view knowledge in science as cumulative; it builds upon existing knowledge as science progresses. They believe we can separate objective truth from our "means of knowing it." In other words the identity of the researcher and the choice of research methodologies will have no effect on the truth that comes out of the research. ... Relativists accept the existence of the world but question whether the world is "knowable." They note that observations, and the choice of observations to be made, are influenced by [the] beliefs, theories, hypotheses, and background of the individual who makes them. Statements about these observations are then expressed in a language whose words are embedded in a particular theoretical framework. Relativists therefore question whether a truly unbiased, objective observer can exist.[15]

I think this is a simply a misrepresentation of realism as well as relativism. To lump together realism, objectivism, and positivism is misleading, as is the implication that these positions are necessarily outmoded and inappropriate. Objectivism and realism, among the three positions grouped together, remain perfectly viable and are supported by the majority of scientists and philosophers of science. One does not need to be a relativist to accept that observations are influenced by the beliefs and background theories held by the observer. Most objectivists or realists would happily concede these uncontroversial claims regarding scientific knowledge.

Contrary to what Bodner and colleagues are claiming, the central idea in relativism is precisely that all knowledge is relative. This implies that the forms of knowledge derived from chemistry, black magic, or voodoo, to take three random examples, are all equally valid. I maintain that anyone who believes that science is

worth teaching, in preference to these other pursuits, would not claim allegiance to this form of relativism. As far as I know, the only person to ever propose such an outrageous view was the self-proclaimed anarchist of science, Paul Feyerabend,[16] who did so in very similar terms. But even Feyerabend, unlike political anarchists, conceded that he did not intend others to take him seriously.

In the world of analytical philosophy, to be accused of being a relativist is tantamount to being accused of violating rationality itself. If all forms of knowledge are relative, why should one accept relativism as a worthwhile view to adopt? Relativism is simply a self-defeating position. I cannot believe that any scientist would seriously contemplate relativism as a viable philosophical position regarding the nature of scientific knowledge, or that science educators would be prepared to accept such a view. And yet this is precisely what Bodner and colleagues are recommending, in the mistaken belief that it represents a more enlightened and up-to-date philosophical approach to science.

But even the more extreme philosophers and sociologists of science who claim to be relativists have been forced to moderate their position in the light of criticism. It appears to have escaped the attention of the chemical constructivists that leading relativists like Harry Collins are now advocating what they term "methodological relativism" as opposed to full-blown, or philosophical, relativism. Collins now holds that

> Methodological relativism says nothing directly about reality or the justification of knowledge. Methodological relativism is an attitude of mind recommended to the social-scientist investigator. the sociologist or historian should act as though the beliefs about reality of any competing groups being investigated are not caused by reality itself.[17]

It appears that even the most extreme relativists are trying to distance themselves from full-blown relativism. Meanwhile the chemical educators quoted above still cling to an extreme version of relativism in the belief that it represents an improvement on "objectivism, positivism, and realism."

WHY THROW OUT THE BABY WITH THE BATHWATER?

To do full justice to the question of constructivism in science education would require a discussion of how this term is used by philosophers, sociologists, and anthropologists on one hand, and science educators on the other hand. It is important to distinguish the radical claims of the constructivists, who maintain that scientific knowledge itself is obtained by a process of negotiation and social forces, from the claims of constructivists in science education.

The first group of authors opposes the traditional belief that scientific knowledge results from investigating the way the world actually is. Meanwhile, the claims made by most constructivists in the educational sphere are more modest. They claim that students develop their understanding of science in a constructivist manner. This process is supposed to involve issues such as the preconceptions and misconceptions that students might bring to chemistry classes. One can, of course, accept such views about learning science while at the same time rejecting the more radical philosophical constructivism that claims that scientific knowledge itself is arrived at by a process of social negotiation.

Fully mature scientific knowledge, of the form that commands widespread consent by the community of scientists, does not differ according to the pedagogical evolution of the particular scientist concerned. Of course, the views of mature scientists may well have begun as "constructions" that might have been influenced by all manner of social factors, but mature science is largely free of personal idiosyncrasies.

If, on the other hand, some chemical educators do wish to support the more radical claim, that mature science itself shares constructivist elements, they should make this more explicit in their writings. But one suspects that only a small minority of chemical educators—most were trained as chemists—would want to go quite so far. Most educators are understandably attracted to educational constructivism, but overstate their case by drawing support from the more extreme and often anti-scientific writings of philosophical constructivists.

Of course, each individual developing student may have a slightly different initial conception of any particular phenomenon. One might also grant that this conception may be relative to the educational and even sociological background of the individual. But the process of learning science, perhaps more than any other field, involves reaching a position where the student has understood enough of the shared store of knowledge so that he or she can communicate with others, and even make contributions to the general scientific consensus.

I applaud chemical constructivists for encouraging teachers to be more conscious of the fact that students come to the study of chemical topics from a great variety of directions. But with respect to concepts such as constructivism and relativism, ideas borrowed from philosophy, chemical constructivists need to make it clear that they are not supporting the same brand of constructivism or relativism in the context of pedagogy. Unfortunately, the present appeal to a nonspecific "constructivism" continues to cause confusion.

SO WHAT?

Some readers may be asking whether any of these philosophical concerns have any real importance in chemical education. I believe that they have great importance, and that chemical education oversimplifies its philosophical content, as I have tried to suggest above. The current approach is sloppy and not conducive to the growth or wider acceptance of chemical education research. It is high time for chemical educators to become more philosophically informed and to begin to address the kinds of issues raised here. Otherwise, they will be providing further ammunition to what scientists generally regard as the "wrong side" of the Science Wars debate.

WHAT SHOULD BE DONE?

What I am recommending is not less use of philosophy in educational issues but more careful use. The obvious remedy is for chemical education researchers to become better acquainted with the philosophical positions to which they appeal in their writings. Secondly, philosophers of science have largely forsaken the search for an all-encompassing account of the scientific method and have concentrated instead on

developing philosophical understandings of each separate natural science. Gone are the days of "heroic philosophy of science," when Popper, Kuhn, or Lakatos would try to pronounce on the nature of the whole of science.[18] It may be because these philosophers attempted to cast their nets too widely that they failed to obtain any lasting criteria to describe the nature of the scientific method.

And yet chemical constructivists continue to base a large part of their work on the views of a Kuhn or Feyerabend, to cite the most popular choices among science educators. Chemistry, like any science, has its own philosophical peculiarities that have been the focus of much investigation since the rebirth of philosophy of chemistry in the early 1990s. But whereas philosophy of chemistry is presently the fastest growing subfield in philosophy of science, it has been almost completely ignored by chemical education researchers, with a few exceptions.[19] Many resources are now available in philosophy of chemistry. All that is required is for chemical educators to begin to draw upon them.[20]

Chemistry is partly a liberal art, and is as much about thinking as it is about synthesis, experimentation, and computation. It is unfortunate that philosophy, which provides the most systematic analysis of ways of thinking, has been traditionally neglected by chemists. Even if chemical educators ignore recommendations that they should take an interest in philosophy, they should at least strive to obtain a good understanding of those philosophical concepts that have already crept into chemical education. Now that the situation has begun to change, and philosophy of chemistry is becoming an established discipline, there is no excuse for shoddy philosophical thinking on the part of chemical educators.

Just as scientists tend to be suspicious of the anti-science lobby in the Science Wars debate, they are also correctly suspicious of chemical or other educators who openly support relativistic views about science. The view that individual students may bring a variety of preconceptions to the study of chemistry is a valuable one, but this should not commit educators to relativistic views about the nature of mature science.

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The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues

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The Recently Claimed Observation of Atomic Orbitals and Some Related Philosophical Issues

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The main thrust of the paper involves a theoretical and philosophical analysis of the claim made in September 1999 that atomic orbitals have been directly imaged for the first time. After a brief account of the recent claims the paper reviews the development of the orbit and later orbital concepts and analyzes the theoretical status of atomic orbitals. The conclusion is that contrary to these claims, atomic orbitals have not in fact been observed. The non-referring nature of modern atomic orbitals is discussed in the context of Laudan's writings on realism, the success of theories, and whether or not scientific terms refer. I conclude that the failure to observe orbitals is a good prima facie case for divorcing the success of theories from the question of whether their central terms refer. The added relevance of this case is that it concerns a current and highly successful theory. Finally, the relevance of this 'floating model' to contemporary discussions on scientific models is briefly considered.

1. Reports Claiming That Atomic Models Have Been Directly Observed. The recent dramatic claims made in *Nature* magazine to the effect that atomic orbitals have been directly observed fly in the face of conventional wisdom regarding the nature of such theoretical entities. Of course this alone does not represent grounds for dismissing such claims. However, if these claims were to be sustained it would imply an outright refutation of quantum mechanics, which does not appear to be the intention of the authors concerned.

Unlike the infamous and recent case of cold fusion, the claims made for the observation of atomic orbitals were not presented at a press conference but, as mentioned above, were announced in the world's most

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prestigious scientific news journal. The front page of this issue of *Nature* featured the simple words "Orbitals observed" in large bold letters, alongside some images taken from the primary article, which states:

> [T]he correspondence between our experimental map and the classical diagrams of d_z^2 orbitals sketched in textbooks is striking. All our difference maps show strong non-spherical charge distributions around the copper atoms, with the characteristic shape of d orbitals. (Zuo et al. 1999, 51)

An accompanying editorial article in the same issue of *Nature* shows less, if any, reservation concerning the identification of the images obtained with textbook orbitals. The headline caption for the editorial begins,

> The classic textbook shape of electron orbitals has now been directly observed. (Humphreys 1999)

This is followed by the statement that

> [f]or the first time the striking shape of some of the electron orbitals is revealed experimentally. The paper by Zuo et al. is remarkable because the quality of their charge-density maps allows, for the first time, a direct experimental 'picture' to be taken of the complex shape of the d_z^2 orbital. (Humphreys 1999, 21)

Other quality science magazines as well as trade journals have shown even less caution in reporting the orbital claims emanating from Arizona State University. A web page produced by a respected popular science magazine states boldly:

> The idea of orbitals has long proved useful for describing atoms and their interactions mathematically, but not physically. Now all that's changed. Researchers at Arizona State University recently published in *Nature* the first true images of atomic orbitals in Cu_2O, a crystal called cuprite. (http://www.sciam.com, 1999)

An article appearing in *Chemical and Engineering News* begins with:

> Remember the really neat-looking d-orbital from freshman chemistry? The one that looks like a three dimensional figure 8 with a doughnut around its midsection? Well, it's just been experimentally observed by Scientists at Arizona State University at Tempe. (Jacoby 1999, 8)

In addition, the primary researchers have insisted, in various quoted remarks, that they are indeed directly imaging "textbook orbitals" rather than mere electron density or computer generated images of orbitals.[1]

1. The lead author from the primary article in *Nature*, J. M. Zuo, is quoted as saying,

Whatever the motivations for such claims might be is not a matter to be entered into in this article. We merely wish to suggest that, as currently understood, in the standard interpretation of quantum mechanics, orbitals cannot possibly be observed.[2]

2. A Brief History of Atomic Orbits and Orbitals. Once upon a time, at the beginning of the twentieth century, several scientists happened on the idea that the structure of the atom might be analogous to that of the solar system, with electrons acting as planets orbiting around the nuclear sun. This idea was first discussed by Jean Perrin in France, while Hantaro Nagaoka in Japan suggested a Saturnian atom with rings of electrons. The now famous experiment performed by Rutherford, on the scattering of alpha rays by a piece of gold foil, provided support for the model of orbiting electrons. Thus the atomic orbit, one of the most enduring metaphors of our age, was born.

Niels Bohr used the notion of atomic orbits in his theory of the hydrogen atom and even gave an approximate explanation for the form of the periodic table of the elements, by appealing to electron orbits in many-electron atoms (Scerri 1997). However, he himself soon realized that such electron orbits in atoms larger than hydrogen would have to be regarded as only useful approximations.

The advent of quantum mechanics at the hands of Heisenberg, Schrödinger, Born, and others provided a more abstract picture of the atom. Now electrons were to be thought of as being in three-dimensional orbitals, in which the change in terminology would denote an important conceptual change. Unfortunately the change in terminology has not been radical enough, with the result that many scientists and educators, at many levels of enquiry, appear to retain a realistic notion for the new concept of an orbital in the sense of electrons undergoing a trajectory. Following Heisenberg the exact location of the electron could no longer be specified. This finding, together with the probabalistic interpretation of quantum mechanics, led to the introduction of probability clouds to represent orbitals. The brief sketch of the historical development of atomic physics is

"It's direct experimental proof of the quantum model." This is in an article entitled "Observing Orbitals", with the subtitle, "The first pictures of atomic orbitals are confirming theories and resolving controversies". In fact it has been articles such as this one that have fueled a new controversy regarding whether orbitals exist physically or not.

2. There has been almost unanimous agreement among participants of several Internet discussion lists that orbitals cannot possibly be observed. These lists include hopos, philchem, chemed, and the history of chemistry server. Professional theoretical chemists do not even see much need for discussion since in their view the issue is quite clear-cut in that orbitals are simply unobservable. Several individual theoreticians whom I have contacted directly agree on this point.

all too familiar. But what is not often appreciated is that Heisenberg's discovery sets limits on the accuracy with which the position and momentum of an electron can be specified but does not rule out an electron trajectory in principle. The result of this confusion is that some people seem to believe that the electron still maintains a definite trajectory but that we merely cannot specify this trajectory precisely. In fact, there are strong reasons for ruling out electron trajectories which do not depend on Heisenberg's principle.

2.1. The Orbital Model As an Approximation. The quantum mechanical revolution also implies a more technical modification to our view of microscopic phenomena. Whereas the old quantum theory, as perfected by Pauli, required the assignment of as many as four quantum numbers to each electron in a many-electron atom, the arrival of quantum mechanics showed that even this more abstract notion is strictly inconsistent in any atom other than hydrogen. This result can be expressed by saying that individual electrons in a many-electron atom are not of themselves in stationary states whereas the atom as a whole does possess stationary states. This change in perspective is far from trivial and shows definitively that the orbital model is an approximation in many-electron systems. It also requires that the scientific term 'orbital' is strictly non-referring with the exception of when it applies to the hydrogen atom or other one-electron systems.[3]

Unfortunately this part of the message from quantum mechanics has not been readily assimilated and many professional chemists and even physicists are still not clear about the issue.

3. The Modern View of Orbitals Among Experts. Even so, the fact that orbitals in the modern sense of the term represent an approximation in many-electron systems does not provide sufficient grounds for my earlier categorical claim that orbitals cannot be observed under any circumstances. I will return to this point in due course. The continuing value of orbitals lies in their serving as basis sets, or a form of coordinate system, with which the wavefunction of an atom, ion, or molecule can be expanded mathematically to any degree of accuracy dictated by the available computational power. Orbitals have not only lost their former pictorial aspect which they possessed at the beginning of the century when they were still called orbits, but now even the mere assignment of electrons to specific orbitals, or electronic configurations, as regularly carried out in chemistry and physics has lost its physical significance. Of course, the orbital model remains enormously useful as an approximation and lies at the heart of

3. For example the ions He^{+}, Li^{+2}, or Be^{+3}.

much of quantum chemistry but it is just that—a model, without physical significance, as all computational chemists and physicists are well aware (Scerri 1991, 2000). Atomic orbitals also serve as a means of classifying spectroscopic transitions in the study of atomic spectra (Condon and Shortley 1935).

In fact, only the atom as a whole possesses well defined stationary states and these states are characterized by the vectorial coupling of individual electronic momenta, with different coupling schemes operating depending on the kind of atom in question.[4] In addition, the usual textbook statements which refer to particular numbers of electrons in particular orbitals, such as 1s, 2p, or 3d orbitals, are in strict violation of the Pauli principle, which maintains that all electrons in the system are indistinguishable. These shortcomings of the orbital concept are counteracted, to some extent, by means of the permutation of all the electrons in the course of Hartree-Fock calculations. If one insists on retaining a physical picture this would correspond to the view that each electron is in every single orbital simultaneously. But even this procedure does not succeed in including the residual and significant effect known as dynamic correlation between electrons. To do so requires the use of more sophisticated mathematical techniques, some of which go beyond the orbital approximation.[5]

In modern theory, atomic orbitals serve merely as basis sets, that is, as forms of coordinate systems which can be used to expand mathematically the wavefunction of any particular physical system. Just as the coordinate system of x, y, and z used to describe any particular experiment in classical physics is unobservable, so too atomic orbitals are completely unobservable even in principle. What can be observed, and indeed is frequently observed in experiments, is electron density.

3.1. Back To the Recent Claims. In the recently announced experiments the authors have fit experimental X-ray and electron diffraction data to a

4. The strictly non-referring nature of atomic orbitals can be expressed through the following mathematical equation:

$$[H, l_x] \neq 0.$$

This states that the operator corresponding to the angular momentum of any particular electron does not commute with the Hamiltonian of the system. As a result, individual electrons are not in genuine stationary states, although the ensemble of all the electrons possess genuine stationary states.

5. The failure to include correlation energy in a typical atomic calculation results in an error of approximately one percent in the total energy of an atom. This may seem insignificant but it is not, especially as typical bonding energies amount to about one percent of total atomic energies. A calculation which fails to include correlation energy can thus fail to predict whether bonding occurs or not between the atoms of any two particular elements.

model called multipole refinement. This method does not assume an actual sum of atomic contributions but fits the data by an expansion in terms of radial functions multiplied by spherical harmonics on various centers. The result is a charge density which is then compared to that obtained as a superposition of spherical atomic contributions, assuming that the compound is perfectly ionic. The density difference map is thus obtained as the difference between the experimental fit and the spherical or purely ionic fit (Coppens 1997; Tsirelson and Ozerov 1996).

My aim is not to deny that the techniques reported may have thus provided an image of overall electron density in the copper compounds in question but only to question whether

> [t]he classic textbook shape of electron orbitals has now been directly observed (Humphreys 1999, 21),

to cite again the editorial in *Nature*, and the suggested linking of the images obtained with 3d orbitals in the primary paper.

Although the primary authors may not have made the explicit claim of having observed atomic orbitals, it seems a little odd that they should have expressed their findings in such a suggestive and, as it has turned out, rather misleading manner. It is also rather odd that in all their quoted remarks which have appeared in other magazines, and even newspapers, the authors have done nothing to deny, or at least diminish, the reports that they have in fact directly observed some orbitals.

I suggest that any similarities between the reported images and textbook orbitals may be completely coincidental.[6] As philosophers are well aware, scientists are often quick to draw realistic conclusions from their experimental findings. However, it is essential for scientists to be more discerning in attributing physical reality to entities which are defined theoretically and which the theory itself informs us do not exist physically. It is also rather unfortunate that popular science journals from which many philosophers and science educators rightly draw scientific information should have misrepresented the recent findings. But as I suggested earlier this is not entirely surprising in view of the way that the results were first communicated.

6. Interestingly, John Spence, the leader of the Arizona State team responsible for the alleged observation of orbitals, has conceded as much in a recent personal correspondence (16 September, 1999) when he writes,

> [M]y own feeling is that there is little chance of educating non-specialists on these issues. The one-electron picture is too ingrained in most scientists' thinking (and too useful in many cases!) to be eradicated. And the fact is that the measured valence charge density (difference) *in cuprite* does actually resemble a d_{z^2} "orbital" hole, however fortuitous that may be.

4. More About the Nature of Atomic Orbitals. First of all the term 'orbital' is a highly generic one. It is used to describe hydrogenic orbitals, Gaussian orbitals, natural orbitals, spin orbitals, Hylleraas orbitals, Kohn-Sham orbitals, and so on. All incidentally are unobservable *in principle*.

The hydrogenic variety of orbitals comes from the exact solution of the non-relativistic Schrödinger equation for the hydrogen atom. I propose to focus on these orbitals since the claim by the Arizona State scientists concerns the observation of 3d orbitals, which represent one kind of hydrogenic orbital. The nature of quantum mechanics is such that it features operators, eigenfunctions, and eigenvalues, and only the last of these are observable. Orbitals are eigenvectors, or more specifically, the components out of which eigenvectors are constructed. In the case in point it is only the values of quantum numbers which can be observed. For example, the specification of a 3d orbital requires the assignment of three distinct quantum numbers, as is well known. These are $n = 3$, $\ell = 2$, and m_ℓ, which can take any of 5 values $(-2, -1, 0, 1, 2)$ depending on which d orbital is identified. In a many-electron atom this type of 3 quantum number (4 if spin is included) description breaks down. For example, in a system where there is no spin-orbit coupling but only Coulombic interactions, that is to say, only electron-electron interactions, it is necessary to consider the vectorial sum of the separate ℓ, m_ℓ, and m_s quantum numbers. The observable corresponding to angular momentum, denoted by capital L, is obtained as a vector sum of the individual ℓ's. But this 'observable' will not correspond to, that is, will not be characteristic of, the shape of a d orbital or even s or p. If anything it will correspond to a composite shape due to contributions from the shapes of all the orbitals. Contrary to the frequently seen textbook representations, the atom does not retain the appearance of a set of concentric orbital shapes consisting of the 1s, 2s, 2p orbitals, etc. In fact they all combine together and there is therefore no reason to expect that the eigenvalues obtained will correspond to an outer envelope with the shape of a d orbital, let alone the supposedly observed $3d_{z^2}$.

The term 'orbital' thus has a specific theoretical meaning and just because the images obtained, following much data processing, roughly correspond to what might loosely be termed 'orbitals' is no reason for making such an identification. Identity does not come in degrees but is an all-or-nothing affair. Those who are suggesting that we should make this kind of identification are guilty of making a category mistake.

5. Orbitals and the Question of whether Successful Theories Imply Referring Theoretical Terms. In this final section I turn to the question of realism and specifically the discussion regarding whether the theoretical terms which appear in scientific theories genuinely refer or not. In fact my aim is more specific since I will be concentrating on whether it is the case that

successful scientific theories imply that the terms employed refer. Here I will be considering atomic orbitals as my main example of theoretical terms.

In order to pursue this question I focus on a much cited article in the literature, namely, Larry Laudan's "A Confutation of Convergent Realism" (Laudan 1981). I will take up some of his points in order to see whether the case of atomic orbitals casts any new light on the issue or whether it might even serve as a different kind of example. I do this because I believe that a stronger case can be made for divorcing the question of whether theoretical terms refer from the question of the success or otherwise of the theories in which such terms are featured.

Laudan asks whether, as a matter of historical fact, successful past theories always possess referring terms in the sense generally taken by realists. He provides numerous examples to show that this has generally not been the case. For example, Laudan cites several ether theories and other influential theories from the eighteenth and nineteenth century, like phlogiston and caloric, which were successful but possessed non-referring central terms from a modern perspective. Laudan does not however venture to make such an argument for any twentieth century theories or even less for any currently accepted theories in science.

Of course in the historical cases cited by Laudan, the realist can claim that the terms may not have referred but that something which survives in the currently accepted theory did refer and that this explains why the older theory enjoyed some previous success. I will return to this 'retention' issue below.

But first I will pursue my main goal. I want to argue that Laudan's case is even stronger than he seems to believe, and even applies to the most successful and far reaching scientific theory which has ever been devised, namely, quantum mechanics. Of course the critic can respond by pointing out that the term 'orbital' is only one of many used in modern quantum chemistry and physics. But Laudan himself has provided a response to those who might doubt whether an argument based on just one theoretical term belonging to any theory should carry any persuasive power in writing:

> After all, part of what separates the realist from the positivist is the former's belief that the evidence for a theory is evidence for *everything* the theory asserts. . . . For realists like Boyd, either all parts of the theory (both observational and non observational) are confirmed by successful tests or none are. In general, realists have been able to utilize various holistic arguments to insist that it is not merely the low-level claims of a well-tested theory that are confirmed but its deep-structural assumptions as well. (Laudan 1981, 226–227)

Put in other words, this implies that if one term fails to refer, this feature has a bearing on the whole theory and cannot be conveniently put to one side.

In any case there is no denying the ubiquity of the theoretical term 'orbital' in modern quantum chemistry. As I mentioned briefly earlier in the article there are many kinds of orbitals such as hydrogenic, Hylleraas-type, natural orbitals, spin orbitals, and so on. Indeed there is hardly any computational work carried out in quantum chemistry which can genuinely be said not to use some kind of orbital method.

It should by now be clear from the preceding sections that the generally accepted view of atomic orbitals is that they are strictly non-referring in that they do not pick out any entity which may be said to physically exist in the same sense that a planetary orbit exists. This does not, however, diminish their usefulness in a multitude of computational schemes employed in quantum chemistry or their applicability to the classification of spectroscopic transitions and to a discussion of a plethora of chemical and physical phenomena. In addition, much of the success of modern quantum chemistry, including the award of the 1998 Nobel Prize for chemistry, is directly attributable to the use of calculations based on atomic and molecular orbitals.

By restricting himself to defunct theories Laudan cannot carry his argument through as successfully as he might. This is because he leaves open the possibility for the realist to claim that successful past theories are always replaced by theories that preserve reference even if the precise nature of the referent changes with the change of theories. This is the argument which sometimes appeals to the example of theories of the electron. It is of no importance, the realist claims, if the electron theory is Thomson's, Rutherford's, or Bohr's since although the precise description of the particle may change the actual referent has remained constant.

I claim that atomic orbitals provide an interesting prima facie case against this view since they began life as well defined referential terms in Bohr's, and even older theories of atomic structure, only to lose their ability to refer with the advent of quantum mechanics. It does not matter whose orbitals are selected from the modern palette of choices since *none* of them refer. The realist cannot therefore claim that reference has been preserved in the same way that she might in the case of electron theories.

It should be noted that at least some philosophers of science do contemplate the possibility of divorcing reference from the success of scientific theories. Such is the case with Hardin and Rosenberg in their critique of Laudan's article that I am considering here (Hardin and Rosenberg 1982). But as Laudan has properly responded, in my view, the price for such a divorce is that it leaves the realist in a position which is hardly distinguishable from instrumentalism and it undercuts any possibility of making in-

ferences to the best explanation, which is the fundamental move bolstering the realist's overall position.[7]

Of course Laudan himself does want to divorce the success of theories from the question of whether their terms are referential. In arguing from cases in defunct scientific theories he is suggesting that this will also turn out to be the case in our current theories. Here Laudan appeals to his "Pessimistic Meta-Induction" to say that all theories will eventually be refuted and their terms will become non-referring. But as many authors have pointed out, the idea of a pessimistic meta-induction itself is open to criticism. It would therefore be advantageous to have a more direct argument for saying that an important term in quantum mechanics is non-referring even before the theory has been refuted. What Laudan has not availed himself of, however, has been any example from present-day highly successful science where the theory itself stipulates that a central term is non-referential. This is what I believe I am providing in this article.

The bottom line would seem to be that if orbitals could be directly observed then the realist would have won the elusive victory, since the term 'orbital' would be shown to be referential. Given the undeniable success of quantum chemistry, the realist would be able to claim that in one very important case, at least, success and genuine reference go hand-in-hand. Unfortunately for the realist camp the claimed observation has turned out to be a chimera. Whereas this fact this does not seem to be of great importance to the primary researchers, I believe that it is rather important to philosophers of science.

Of course if by some miracle it emerges that orbitals have after all been observed in the recent experiments, or any future ones for that matter, then all the arguments I offer here to disconnect the success of quantum mechanics from whether its terms refer will have collapsed completely. It is for this reason that I think that the recent claim deserves far more critical scrutiny than it has received up to now.[8]

6. Conclusion and the Question of Models. Recent work by philosophers seems to place less emphasis on linguistic aspects of theories as well as on the questions of realism and anti-realism and whether or not scientific terms refer. The modern approach has been to attend to semantic aspects of scientific theories, and most importantly, to examine the role of models within scientific theories. In view of this tendency it becomes all the more relevant to obtain a clear understanding of the status of one of the central

7. The 'no divorce' view which Laudan attributes to most realists is to be found expressed in the writings of Putnam, Boyd, and Newton-Smith, among others.

8. Up to the time of writing, I am not aware of a single critical evaluation of this episode in the philosophical literature.

models used in chemistry and physics, namely, the atomic orbital model or the independent-electron approximation as it is also termed.

Moreover, philosophers who are interested in models might want to consider a rather curious feature of the orbital model. I am referring to the fact that the orbital model has been called a 'floating model'. This term, first coined by Heinz Post (1974), aptly describes the somewhat ambiguous nature of atomic orbitals. The model is said to float because it is neither securely anchored theoretically nor empirically. As was described earlier, orbitals are not strictly derived from quantum mechanics in the case of many-electron systems. The approximation involves assuming that each of the electrons in a many-electron system moves in a resultant field consisting of the nucleus and all the other electrons apart from the one being considered.[9] In this approximation one can return, approximately, to considering a many-electron system as a pseudo one-electron system. Only then can one return to using the 1s, 2s, 2p and other familiar orbital labels for solutions to the hydrogen atom problem which *do* have a secure basis in theory.

From the experimental side the floating nature concerns the fact that only quantum states, or more correctly, only transitions between such quantum states, are truly observable. Electronic configurations that are specified in terms of the occupation of atomic orbitals do not correspond to quantum states *except* in the case of the hydrogen atom. The measurement of atomic orbital energies in the case of atoms and molecules is generally carried out via the Koopman theorem, which states that the orbital energy is equal to the negative value of the ionization energy of any particular electron.[10] But this too is an approximation since it depends on the counterfactual assumption that, on the removal of any particular electron from an atom or molecule, the remaining electrons do not experience any relaxation resulting from the resultant dynamical situation.

The newly announced experiments, like several others reported in recent years, may indeed show images of electron density, or differences in electron density, but not atomic orbitals, regardless of the claimed sophistication of the experimental techniques employed. I suggest that any similarities between the reported images and textbook orbitals are coin-

9. This is called the central field approximation or the Hatree-Fock model.

10. Koopman's theorem states:

> The energy, I_r, required to remove an electron from an orbital Ψ_r, on the assumption that the other electrons do not adjust their distribution, is the negative of the one electron orbital energy ε_r
>
> $$I_r \sim -\varepsilon_r.$$

This so-called theorem is only an approximation because electrons do in fact relax into a new distribution on the removal of an electron.

cidental or results of theory-laden analyses of the data obtained. Both the *Nature* editorial feature by Humphreys and the primary article itself are mistaken in claiming, or strongly implying, that d orbitals have been imaged for the first time.

6.1. The Real Crux of the Matter. I have kept till last the most categorical reason for wanting to deny the possibility of ever observing an orbital. After all, the fact that orbitals might only provide an approximation to the motion of many-electron systems is not a sufficient reason for the complete denial that they or something related to orbitals can possibly exist. My final argument, which I claim to be the most decisive one, is that orbitals depict a quantity called probability amplitude, which has been known to be unobservable in principle since the birth of quantum mechanics as distinct from the old quantum theory.

Whereas the amplitude associated with classical wave motion such as sound waves or water waves corresponds to the 'height' of the crest of the wave, this is not so in the case of matter waves of which electron waves are an example. Here the term 'amplitude' is only used by analogy. For example, the intensity of a matter wave, or even a light wave, is not proportional to the square of the amplitude of the wave. This much has been known since Einstein's elucidation of the photoelectric effect in 1905 when it emerged that the energy of the X-rays which produce the photoelectric effect is proportional to their frequency and not their amplitude. The terms 'amplitude' and 'orbital' as used in quantum mechanics, with reference to matter waves, are both somewhat misleading since they wrongly suggest analogies with classical amplitudes or classical trajectories. An electron has neither of these classical properties and, most crucially for the purposes of the present paper, has no classical trajectory. Moreover the mathematical expression for most atomic orbitals involves the number i , (the square root of minus one), thus rendering the number imaginary. This is why one can only observe the square of an atomic orbital rather than the atomic orbital itself. The square of the square root of minus one is, of course, minus one, which is physically meaningful unlike i, which is imaginary. Or to state a general result of quantum mechanics which goes beyond just talk of orbitals, the wavefunction for any system is unobservable whereas the square of the wavefunction can be observed, since the act of squaring turns an imaginary quantity into a real one.

And if this was not enough it emerges that atomic orbitals are described in a many-dimensional Hilbert space which defies visualization since we can only observe objects in three dimensional space. How then can anyone still claim that orbitals have been directly observed? And yet this is just what was claimed in *Nature* magazine and many other journals without

the subsequent appearance of a single letter to the editor to contest this claim.

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CHAPTER 6

NORMATIVE AND DESCRIPTIVE PHILOSOPHY OF SCIENCE AND THE ROLE OF CHEMISTRY

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INTRODUCTION

Since the demise of Logical Positivism the purely normative approach to philosophy of science has been increasingly challenged. Many philosophers of science now consider themselves as naturalists and it becomes a matter of which particular variety they are willing to support. As is well known, one of the central issues in the debate over naturalism concerns whether philosophy offers a privileged standpoint from which to study the nature of science, or whether science is best studied by studying science itself.[1]

The situation is often summarized by the aphorism that one cannot derive an "ought from an is." It does not appear as though we should be entitled to draw normative conclusions about how science should ideally be conducted by merely observing the manner in which it is conducted at present, or was conducted in the past, since this appears to be a circular argument. Indeed the only circumstance in which the die-hard normative epistemologist would contemplate any input from naturalism would be if it could be shown conclusively that rational agents were literally incapable of thinking in the manner which the normative scheme requires that they should.[2]

I am speaking as though the normative approach is somehow more respectable and that naturalism represents a recent intruder onto the philosophical scene. I am suggesting that the burden of proof lies with the naturalists to show that their position can have some influence on normative philosophy and not vice versa. This may indeed be the case at the present time but things were not always this way. Normative philosophy and philosophy of science did not always hold center stage. It arose as a result of the work of Gottlob Frege in Jena at the end of the 19th century. Frege's development of modern logic rapidly led to attempts to base all of philosophy on the analysis of language, a program that was furthered by Russell, Wittgenstein, Carnap, and many others. Frege's program led to the overthrow of the then current naturalistic philosophy, which looked to scientific discoveries and scientific practice for philosophical enlightenment.

Before Frege, the study of psychology and evolutionary biology *were* indeed highly regarded among philosophers of the day. In particular, psychologism was not

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considered to be the 'mortal sin' that Frege later convinced analytical philosophers that it might be.

Today confidence in the analysis of the logical structure of scientific theories and the approach involving an *a priori* or a "first philosophy" has waned. Philosophers *do* now explore ideas from psychology, biology, physics, political science, economics, computation, and as it would appear are even beginning to consider the field of chemistry (van Brakel 2000; Bhushan and Rosenfeld 2000). These excursions may all be said to fall under the generic label of naturalism. The proponents of these approaches share an opposition to the Frege–Wittgenstein line whereby philosophy is somehow more fundamental than all these other branches of learning.

I want to spend a few more moments in exploring how the stranglehold that Frege had around analytical philosophy has been loosened. Frege's position may be stated in simple terms as requiring that:

(i) Logic and not psychology is the proper medium for philosophy.
(ii) Philosophical reflection is to be regarded as *a priori*.

Modern naturalists, not surprisingly, dispute both (i) and (ii). One of the main reasons why (i) has been reconsidered, and why there has been a return to psychologism, has come from work in epistemology. In 1963, Edmund Gettier presented some examples to show that there are cases when one might possess true and justified belief and yet fail to have knowledge (Gettier 1963). Philosophers like Dretske and Goldman have led the way in formulating responses to these puzzles that invoke the psychological states of knowing agents (Dretske 1981; Goldman 1992).

Meanwhile (ii) has been challenged on various fronts. First of all, Quine produced his famous articles in which he argued that the distinction between analytic and synthetic statements could not be clearly drawn (Quine 1951). As a result, any hopes of a completely *a priori* approach to philosophy would appear to be discredited. And yet in spite of other well-known contributions from Quine such as his slogan that "philosophy of science is philosophy enough," and his general support for a naturalized epistemology, his own work remained steeped in logical analysis and did not shown much sign of engaging in an examination of actual science.

Then came the historical turn in philosophy of science due to Kuhn, Lakatos, Toulmin, Feyerabend, and Laudan among others. These authors have done much to show the importance of the history of science to the study of scientific methodology. In addition, for better or for worse, the writings of Kuhn, in particular, have spawned the sociology of science and science studies industries which claim to study science as it is actually practiced and stress the need to go beyond an analysis of theories. I say for better or for worse because, as I see it, the problem with sociology of science has been an obsession with the context of scientific developments and the demotion of the actual science involved.[3] What many of these authors have done is to take naturalism a little too far such that they end up with relativism. This is of course one of the well-known dangers of naturalism in general.

Two leading current proponents of naturalism include Ronald Giere and Larry Laudan (Giere 1985, 1989; Laudan 1987, 1990). Perhaps, the main distinction between

them seems to be that Laudan insists that his brand of naturalism is also normative whereas the claim to normativity is rather weaker in Giere's version, although not altogether absent as some commentators seem to believe.

Another author to champion naturalism has been Philip Kitcher. His 1992 article in the centenary issue of *Philosophical Reviews* presents one of the clearest accounts of the history of naturalism and the various currently available positions (Kitcher 1992). Kitcher followed this with a book called *The Advancement of Science* in which he claimed to be doing naturalistic philosophy of a moderate kind. But as some critics have suggested Kitcher seemingly fails to deliver the goods (Solomon 1995). The book is full of formal analysis of scientific episodes such as the Chemical Revolution and one cannot help wondering, as in the case of Quine's writings, where the real science might be lurking.

Of course there are still many philosophers, including Siegel and Doppelt for example, who continue to dispute the very notion of a naturalized philosophy of science (Siegel 1985, 1989; Doppelt 1990).

CHEMISTRY?

So much by way of introduction but what is the relevance of chemistry to these issues? First of all, if by naturalism one means looking at science itself, rather than purely operating within a logical analysis of concepts, then here in chemistry is a whole field of science that has never been seriously considered. The apparent disdain for chemistry is all the more surprising when one considers that chemists are by far the largest group of scientists among people studying and working in any of the sciences.[4]

But the main point I want to make in this article is that in a sense one *can* indeed derive "an ought from an is," although I intend this claim in a more restricted sense than usual. I will argue that by starting with a naturalistic approach to the nature of chemistry, we can make normative recommendations to chemists and chemical educators. The larger question of whether one may make normative claims about science in general is a more difficult one, which I will avoid for the time being. But if what I say about chemistry is correct then perhaps it could easily be generalized to other branches of science (Siegel 1985, 1989, 1990; Doppelt 1990).

FROM NORMATIVE TO NATURALISTIC

I have begun to realize that my own research in philosophy of chemistry has consisted in a gradual shift from initially advocating a normative view about such issues as atomic orbitals and electronic configurations, to more recently adopting a naturalized position. I now find myself advocating the critical use of such concepts rather than highlighting the fact that they strictly fail to refer to any entities in the physical world. Please allow me to now re-trace some of these steps in my own research.

In the case of a many-electron atom or molecule the commutator involving the Hamiltonian operator and the operator corresponding to the angular momentum of an individual electron, [H, ℓ_x], is non-zero. This implies that eigenvalues corresponding to the angular momentum operator for any individual electron is not a constant of the motion, or to use the jargon, is not a good quantum number, and cannot be said to characterize the motion with any exactness. For example, in the absence of spin–orbit coupling only the vectorial sum of all the individual angular momentum operators or L, rather than individual angular momenta, or ℓ, represent good quantum numbers. Another way of stating this result is to say that the individual electrons in a many-electron atom are not in stationary states but that only the atom a whole possesses stationary states. Similar arguments can be made for other quantum numbers like m_ℓ and m_s and these likewise imply the strict breakdown of the notion of assigning four quantum numbers to each electron in many-electron systems.

But more important than the approximate nature of the orbital concept is the categorical fact that an orbital does not refer to any physical entity. Here we are fortunate in having a clear-cut case where it is not left to one's philosophical prejudices as to whether we should adopt a realistic or anti-realistic interpretation. The mathematical analysis dictates quite categorically that the much beloved, and much pictured, concept of atomic orbitals does not have a "real" or independent physical existence. Indeed the use of the term "orbital" rather than orbit does not really convey the radical break with the notion of a continuous path for elementary particles, which took place as a result of the advent of quantum mechanics.

Of course it is still possible to use the complex mathematical expressions, corresponding to the different type of orbital solutions to the hydrogen atom problem, in order to build up a wavefunction that approximates that of a many-electron atom or molecule. In such cases, we are using orbitals in a purely instrumental fashion to model the wavefunction of the atom or molecule and there is no pretense, at least by experts in the field, that the constituent orbitals used in this modeling procedure possess any independent existence. Contrary to the recent claims which appeared in Nature magazine, as well as many other publications, orbitals have not been observed (Scerri 2000b, 2001).

Now what I have been arguing concerning orbitals, for several years, is a normative claim which emerges from paying strict attention to quantum mechanics. But soon after I started to publish these ideas, Robin Hendry, pointed out that according to some philosophical analyses of scientific theories my position was somewhat passé.

Hendry's criticism of my article of 1991 went something like this.[5] He claimed that the issue I was raising did not have quite the philosophical significance that I was attaching to it. Whereas I was pointing out that the realistic interpretation of one-electron orbitals was strictly inconsistent with quantum mechanics, Hendry claimed that in making this assessment I was working within the covering-law model of explanation. This model appeals to fundamental laws for explanation or, in the case I am considering, the Schrödinger equation. Hendry's view, following Nancy Cartwright, was that it is not fundamental theories or laws that explain but scientific models. Of course this represents another version of naturalism. Nancy Cartwright has championed the view that it is models, rather than scientific theories, that are

used in scientific practice to give explanations for natural phenomena (Cartwright 1983).

To connect this with my main theme, I am saying that my own normative approach has been to claim that the fundamental theory explains everything. Hendry countered this claim by appealing to Cartwright-style naturalism which required that we look carefully at the way that models are used. As Cartwright correctly points out, it is often models that scientists appeal to rather than high-level theories. From the normative perspective based on the theory there is indeed something wrong with the way in which the orbital approximation is used in many areas of chemistry and even applied physics. But from the perspective of what I shall call Cartwright–Hendry naturalism, scientists regarding orbitals realistically cannot be faulted given the central role of models in modern science. I did not readily accept this criticism at the time when Hendry first circulated his manuscript but recent developments in my work have now shown me that he was making a very valuable point (Hendry 1994).

In addition, some chemical educators have reacted to my work by pointing out that orbitals are here to stay and that no amount of nit-picking about whether or not they exist physically will have the slightest impact on their use in teaching chemistry (Richman 1999a,b; Emerson 1999). Of course my thought had never been that we should do away with orbitals but that we should point out more carefully their limitations in the course of teaching chemistry.[6] From a philosophical point of view the aim was to examine objectively the theoretical status of electronic orbitals and configurations from the perspective of quantum mechanics.

Then one day some years ago while giving a lecture on philosophy of chemistry a thought came to me. The thought was that it is quite appropriate for chemists and chemical educators to not only use orbitals but to do so in a realistic fashion regardless of their status according to the fundamental theory of quantum mechanics. I think, I fully realized at this moment the truly paradoxical situation in that chemistry is an autonomous science while at the same time resting on fundamental physics. These two positions need not be seen as being contradictory just as the normative and the naturalized position need not be seen as contradictory.

In 1997, I met Bernadette Bensaude, the well-known French philosopher of science, whose work is motivated by the history of chemistry. We struck up a conversation about Paneth and his view of the elements which is the subject of one of the classic papers in philosophy of chemistry written in German and translated by his son Heinz Post (Paneth 1962)[7]. The gist of Paneth's paper is that the chemist must adopt an intermediate position between the fully reductive view afforded by quantum mechanics and a naively realistic view that dwells on colors, smells, and such-like properties of macroscopic chemistry. In that paper, Paneth is concerned with how elements are to be regarded and he upholds a dual view of elements as unobservable "basic substances" on one hand and observable "simple substances" on the other. This he claims resolves a major puzzle in the philosophical understanding of substance, namely how it is that an element can survive in its compounds although the properties of the compound appear to bear very little resemblance to those of the element.

I suggest that this is a way of seeing the relationship between a normative view, or what quantum mechanics says about chemistry, and the more naturalistic view

which tries to consider how chemists and chemical educators actually regard chemical concepts and models. Although it may seem paradoxical to embrace both positions at once, perhaps one might rest easier with Paneth's view of an intermediate position. But my emphasis, contrary to Paneth's conciliatory stance, is that both positions should be adopted simultaneously. Admittedly the history of paradox has a long history in Western thought. Usually a paradox is regarded as a serious problem that must be struggled against and overcome at all costs. Interestingly in Eastern thought, especially Chinese philosophy, paradoxes are not serious dilemmas to be resolved. Instead a paradox is to be embraced for what it is. It is in this rather esoteric sense that I am proposing to regard the reduction of chemistry, on one hand, and the continued use of reduced concepts as being paradoxical.[8]

In the 1960s and 1970s, Kuhn and others showed philosophers of science that it was futile to insist on a normative view of scientific theories which did not bear much relationship to the historical development of real science. Similarly, the case of atomic orbitals, which I continue to concentrate upon, shows us that it is somewhat unhelpful to insist only on the normative view from quantum mechanics. One needs to also consider what is actually done in chemistry and the fact that chemists get by very well by thinking of orbitals are real objects. In fact we need both views, the normative and the descriptive. Without the normative recommendation orbitals are used a little too naively as in the case of many chemical educators who do so without the slightest idea that orbitals are strictly no more than mathematical fictions. Hopefully my previous work was not in vain if I have managed to convince some people in chemical education to be a little more careful about how far an explanation based on orbitals can be taken.

To make a general point now, I think it is still of great value to question the status of the orbital approximation even if one eventually returns to using it in a realistic manner in chemistry. This is because the eventual use of the orbital approximation is greatly improved by such questioning.[9]

FROM NATURALISTIC TO NORMATIVE: THE REDUCTION OF CHEMISTRY

There is another area in philosophy of chemistry where I have been urging a naturalistic approach ever since the beginning of my work. This concerns the question of the reduction of chemistry to physics or more specifically quantum mechanics or relativistic quantum mechanics if one insists on being very precise.

As far back as the 1994 PSA meeting in New Orleans I suggested that the reduction of chemistry should not be regarded in the classic fashion of trying to relate the theories of chemistry to the theories of physics or in the formal sense of seeking bridge principles (Scerri 1994). The problem with such a Nagelian approach is that it requires axiomatized versions of the theory to be reduced as well as the reducing theory. Now although a case can be made for the existence of axiomatic quantum mechanics, clearly the same cannot be said for chemistry since there is no axiomatic theory of chemistry.[10]

But my main reason for advocating a naturalistic approach was that scientists themselves have an entirely different approach to the question of whether chemistry

has been reduced to physics. Instead of considering a formal approach linking the theories in both domains a scientist would try to examine the extent to which chemically important quantities such as bond angles, dipole moments and the like can be derived from first principles from the reducing theory or quantum mechanics. A more challenging question for the theory is whether the liquidity of water, for example, can be predicted from first principles. One suspects that this will remain unattainable for some time to come or even than it may never be achieved. Rather than seeking a relationship between theories, a naturalistic approach to the question of the reduction of chemistry should examine the relationship between chemical properties on one hand and the reducing theory on the other hand.

Of course the hope is to go beyond data such bond lengths or dipole moments and to be able to calculate the feasibility or rate of any particular reaction from first principles without even needing to conduct an experiment. It should be mentioned that considerable progress has been made in the quantum theoretical approach to reaction rates although very accurate treatments have, not surprisingly, been confined to such reactions as that of hydrogen atoms with hydrogen molecules.

Since making this proposal I have found many instances of philosophers who have hinted at precisely this more naturalistic, more pragmatic, approach to reduction which consists in following what computational chemists and physicists do (Suppes 1978; Popper 1982; Hacking 1996). To repeat, whereas philosophers have previously viewed reduction as a relationship between theories, the naturalistic approach I advocate consists in accepting the scientific approach to the reduction of one branch of science to another but without sacrificing any philosophical rigor in analyzing the procedures used. Indeed what begins as naturalism can, I claim, turn to making specific normative recommendations to practitioners in the fields such as computational quantum chemistry (Scerri 1992a, b; 1998a, b). What I discovered was that in many instances in computational quantum chemistry chemists were claiming strict deduction of chemical facts from the Schrödinger equation. But such treatments frequently involved semi-empirical procedures such as using a set of orbitals that are found to work in other calculations or the use of calculations that fail to estimate rigorous error bounds (Scerri 1997). I will not enter into further technicalities here. But I want to suggest is that this is an example of moving in the opposite direction. What begins as a naturalistic or descriptive project ends up by making normative suggestions.[11]

CONCLUSION

I am suggesting that both the normative view about the status or orbitals according to quantum mechanics, and the adoption of a realistic view of orbitals can happily coexist. This I claim is an example of the coexistence of the normative and naturalistic approaches to philosophy of science. This claim will only appear to be a contradiction if one maintains the usual static view about holding philosophical positions. There have recently been signs that philosophers have grown tired of the never-ending arguments regarding realism and anti-realism since they realize that both positions show many virtues. Arthur Fine has coined the phrase "Natural Ontological Attitude"

(Fine 1986). On my reading the important part of this notion resides in the choice of the word "attitude" rather than position and although Fine has not really developed a distinction between attitude and position his articles hint in this direction. What I believe Fine is getting at is that we should no longer think of the discussion as an either/or situation between realism and anti-realism but rather that scientists adopt both positions at different times and sometimes even both at once. These are not so much positions held by scientists and philosophers but the more temporary, more dynamic, attitudes.

I think that this suggests an even further stage in the kind of bootstrapping I have been urging in this paper. The nature of chemistry, more than physics or biology perhaps, could serve as a model for the kind of philosophical approach based on "attitudes" rather than hard and fast positions which one is typically supposed to maintain and defend at all costs. This seems especially appropriate since chemistry, as its practitioners, as well as chemical educators know only too well, requires us to operate on many different levels simultaneously. It demands the adoption of several attitudes. To show you what I have in mind let me end by quoting from the work of a South African chemical educator Michael Laing:

> The difficulty arises because we teach chemistry simultaneously on four different levels, The Realities of Water.
>
> Level 1: macroscopic: tactile (touchable, tasteable, wet to the touch).
>
> Level 2: communicative: language, name: (a) oral and aural, the word, the sound assigned to something that can be seen and felt; and (b) the written version.
>
> Level 3: symbolic, representational: elemental formulaic. This came once chemists understood the concepts of elements, atom, equivalence, valence, stoichiometry, beginning n 1800 and understood by 1860 as confirmed at the Karlsruhe conference. Wet water now becomes H_2O with a relative molecular mass of 18 units. Numeric calculations become important.
>
> Level 4: Atomic scale model. This representation depicts the shape and size of the molecule on a scale so small that it s beyond the comprehension of the average person....
>
> To appreciate water as a chemist you must make use of all four conceptual levels and be able to switch from one to the other as appropriate (Laing 1999).

Chemistry is a fertile new area in which philosophy of science could investigate further the question of normative and naturalistic approaches or the question of whether or not scientists actually adopt philosophical positions in the manner in which they use and interpret scientific theories. My own feeling is that chemists, in particular, tend to adopt different "attitudes," to use Fine's phrase, depending on what level they are operating at.

NOTES

1. The term naturalism has a variety of meanings. For example, in the philosophy of the social sciences it is sometimes taken to mean positivism. This is not the sense in which naturalism is being used in the present article. I am not concerned here with an empirical approach to social science but with a form of naturalism that involves concentrating on the apparatus, techniques, and assumptions of the natural sciences.

2. I am grateful to Martin Curd or Purdue University for discussion on this point.
3. An analogous situation exists in chemical education research at present with nearly all efforts being directed toward the learning process and virtually none at the content of chemistry courses (Scerri 2003).
4. Even sociologists of science appear to have overlooked chemistry, with the possible exception of Bruno Latour's book laboratory life, which is based on observations made in a leading biochemical laboratory (Latour and Woolgar 1979).
5. The article in question is Scerri (1991).
6. In addition, contrary to what Hendry claimed in his article I did not advocate the use of more rigorous forms of quantum chemistry for chemistry at large.
7. See Ruthenberg's short biography of Paneth (Ruthenberg 1997).
8. Needless to say I am not an advocate of parallels between modern science and Eastern mysticism as popularized by the likes of Capra and Zukav (Capra 1976; Zukav 1979). For example see my critique of the alleged parallels between Eastern mysticism and modern physics as published in the American Journal of Physics (Scerri 1989).
9. A recent article by Lombardi and LaBarca analyzes my position on the status of atomic orbitals as well as building on my view (Lombardi and LaBarca 2005).
10. This has not prevented philosophers from trying to axiomatize certain parts of chemistry, such as the Periodic system of the elements for example (Hettema and Kuipers 1988). See also the following critique of these attempts (Scerri 1997).
11. Let me also mention that Paul Needham has produced a detailed critique of my view on the reduction of chemistry in a debate between us which has been published in several issues of the International Journal for the Philosophy of Science (Scerri 1998b; Needham 1999; Scerri 1999; Needham 2000; Scerri 2000a).

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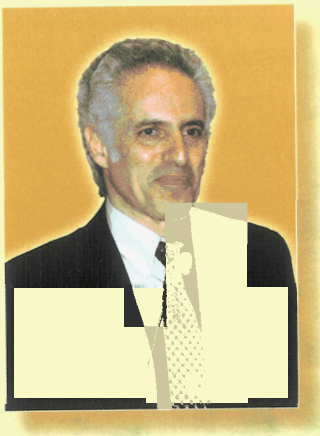

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